

MODERN PETROLEUM REFINING PROCESSES



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PREFACE

The most prolific and dynamic industries of this century are the Petroleum and the Petrochemical. Mankind consumes more than 2,500 million tons of oil yearly. This significantly reveals the magnitude, economic edifice and necessity of the industry. From the most primitive methods of extraction and refining of petroleum, a great transformation has occurred throughout these years to materialise the modern refinery. This is due to the timely induction of the scientific and technological advancements into refinery operations. Advancements are many and knowledge is expanding, one has to keep abreast with these things.

This book describes refinery processes in a concise manner for students. Further, a reference is made to the Indian Petroleum Industry, wherever useful. An attempt is made to use SI units wherever possible.

I acknowledge my indebtedness to publishers like, McGraw Hill, Marcel Dekker, Gulf Publishing Co., Brooks/Cole publishing Co., and journals like Oil and Gas ; Trans of A.I.Ch.E. for their generous cooperation in permitting use of certain data.

Further, I acknowledge my deep sense of gratitude to the Ministry of Petroleum, Chemicals and Fertilizers (G.O.I.), and former Assam Oil Com., for providing me with some useful information.

There remains my pleasant duty to thank Mr. Raju Pramlani, General Editor of Oxford & IBH Publishing Co., Calcutta, for his sincere efforts in bringing out this volume under the series of IIT, Kharagpur—Oxford & IBH Series.

Suggestions to improve this volume are welcome.

B. K. Bhaskara Rao

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CHAPTER 1

Origin, Formation and Composition of Petroleum

1.1 Origin and Formation of Petroleum :

Today, most of the countries in the world are importers of energy. The fossil fuels, accumulated over aeons of geological activity are irreversibly consumed at a rate more than million times faster than they were formed. This has left us in a precarious position especially for petroleum and its products. The hike in price of petroleum and its products, both in national and international scenes is frequent for two simple reasons; the mounting demands and fast depletion of reserves. The importance of petroleum in present day civilization is ever increasing due to its unmatched contribution for our energy requirements, in lubrication and in petrochemical field. Thus its competence to serve mankind is unquestionable and unique too. Sixty percent of the energy needs of the world are met by petroleum. The advent of I.C. and Jet engines have revolutionised the techniques of motive power, a fact, without which the rumbling civilisation would have to contend with a snails-pace. Such a premium stock of limited resources is fast depleting, perhaps due to indiscriminate and wanton consumption. The important question today is how long can the reserves meet the demand even with sky high prices? The high degree of conservation and restrictions in consumption may draw out the global reserves to another century at the consumption rate of today. Then, what?

According to Mayer and Hocott "There is no dearth of petroleum and natural gas resources remaining in the earth. As a matter of fact, there is no foreseen shortage of available sup-

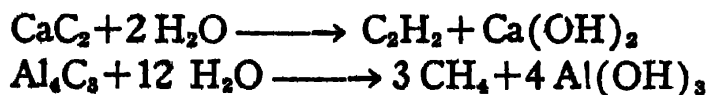
plies by present technology until well into the next century".^{1(a)} Of course, every effort is made to locate new prospective fields, and innovation in search of secondary recovery techniques to lift the oils from existing sources, and what are presently uneconomical fields, is in progress. The controversies may be subdued by understanding the formation of petroleum, at least to some extent. Perhaps resources may not be the problem, but availability may be.

1.1.1 OCCURRENCE OF PETROLEUM

Petroleum occurs in the earth's crust, in all possible states and varies in colour from light brown to dark brown or black, exhibiting luminescence in some cases. It is a mixture of various hydrocarbons, of homologous series namely paraffins, naphthenes and aromatics. Thus the main elements are C (84-86%) and H₂ (11-14%) and other elements O₂, N₂, S rarely constitute about 8%, including different metals in traces. Petroleum is more homogeneous than coal and occurs mostly in sedimentary rocks.

1.1.2 ORIGIN AND FORMATION

Scientists till now are entangled with the problem of explaining successfully the origin and formation of huge hydrocarbon deposits and notably a sound theory has yet to be evolved. Mendeleeff and Berthelot, were caught up with the idea of explaining reasons for such deposits. Their explanation was based upon the inorganic reactions, mainly on the activity of acetylene series. Some carbides produce hydrocarbons when reacted with water, such as



Assuming the availability of such carbides in earth's crust, they arrived at this axiom; in fact, the deposits of such magnitudes could never be balanced with these ideas.

The cosmic hypothesis of V. D. Sokolov depicts that the hydrocarbon vapours were already in cosmic clouds. Favourable conditions leading to precipitation of these clouds, rained hydrocarbons, which were either adsorbed or entrapped in earth's crust.

A doctrine may possibly be explained if ever man comes across such giant deposits in a distant planet, where there happened to be no life at all.

Truly speaking, hydrocarbon vapours are present in certain planets. Hoyle cited the presence of hydrocarbons in the atmosphere of Venus.² These hydrocarbons must be distinguished from the earthly deposits, as purely derived from inorganic materials. Different and conflicting theories appeared in large number to explain the formation of petroleum deposits. The inorganic basis of petroleum formation had to be given up in favour of organic theory due to the following observations and facts as enumerated by J. D. Haun^{1b} :

(a) The homologous series present in petroleum are found only in organic matters.

(b) Nitrogen compounds in petroleum, especially plant derived porphyrins, comprise a very small amount but their significance is immense in the formation of petroleum from life source.

(c) The range of radio isotopes of carbon C^{12} - C^{13} is within the ranges of natural Carbonaceous materials and not from inorganics, as they do not have any chance to absorb radioactivity.

(d) Optical activity, a pre-requisite of natural organics, is exhibited by petroleum.

(e) Petroleum formation is a result of low temperature activity only.

(f) Petroleum is always associated with sedimentary rocks, (even recent formations too) and not with igneous rocks.

(g) Small quantities of petroleum (hydrocarbons) in recent sediments suggest, that the formation of petroleum is normal, continuous and does not require any severe physico-chemical conditions.

(h) Most organisms, like diatoms are found in petroleum.

1.1.3 ORGANIC THEORIES

Engler (1886) was of the opinion that the large marine animals, which dwelt on the globe in the pre-historic days were the main fat contributors. After the natural extinction of these mammoths, the body fat was slowly converted to hydrocarbons, as per his version. But the laboratory experiments revealed that the conversion of fat by hydrolysis yielded only acids and not

hydrocarbon gases. Further, surprisingly no oil well was ever sighted with any fossil remains of such animals. This is how the long flourished hopes of this natural fat theory had to be given up.

There are other schools of thoughts concerning the origin and formation of petroleum; some of which are listed below:

Thomas-Graham (1843) was of the view that natural naphtha must be a product of action upon vegetable matter of high temperature. Chaptal (1845) was of the opinion, that when plants became entirely decomposed into vegetable moulds these contained certain oils which escaped decomposition. J. W. Draper (1846) suggested the action of natural heat of earth on coal. Popoff (1875) showed that methane could be produced by decomposition of cellulose. Hoppe-Seyler in 1886 showed that bacteria could produce methane, as is ever evident in swampy areas. Treibs (1934) discovered some of the plant pigments and biological matter in crudes; micro-scopic organic remains found in crudes actually prompted API to launch a big project API 43 to investigate thoroughly.³

A bright explanation by Mikhailovosky, N. Potering and N. C. Anderson seems to be near the goal. Accordingly, the source of petroleum was not a definite species of flora as initiated by Engler, but the organic matter of sea oozes consisting of remains of plants and animal organisms. The initial decomposition of the vegetable and animal matter is a result of activity of micro-organisms; later the organic matter underwent changes due to pressure and temperature of the crust of the earth. Emphasizing the fact, Arkhagelskey, prophesied that petroleum took birth in argillaceous rocks enriched with organic matter and later migrated and got stored in arenaceous rocks. The extension works of P. Trusk and G. Petrov in U.S.A. characterised the composition and content of organic matter in rocks of different ages. Controversies always flare up, one school advocates—temperature—pressure distillation or by tectonic stress. Another school advocates as a biochemical process; yet another sees it purely as a chemical or radioactivity reaction—and so on. However, biochemical^{4-a} theory has been received with some favour, as it is concerned with low temperature and pressure, and bacteria of versatility. Thus it may be concluded that the

formation is via a combination of physical and biological processes rather than individually. Petroleum formation^(7a) from organic mass may be expounded by two distinct processes namely physical and biological.

1.1.4 PHYSICAL METHODS

It conjures all the parameters in an ideal reaction and depends upon the factors like :

- | | |
|-----------------------|--------------|
| 1. Heat. | 2. Pressure |
| 3. Heat and pressure. | 4. Catalysts |
| 5. Radio activity. | |

1.1.5 BIOLOGICAL METHODS

All the biologic methods are governed by source and environments such as :

1. By preservation of hydrocarbons synthesised by the source sediment organisms.
2. Biological reduction (anerobic or aerobic) sources being :
 - (a) Fatty acids,
 - (b) Proteins and amino acids,
 - (c) Carbohydrates.
3. Biological and Physical methods, such as
 - (a) By condensation of bacterially produced methane under high pressure and temperature in presence of catalysts.
 - (b) By bacterial modification of sediments.

API 43—(A.B.C.) completely relates to the transformation of organic material into petroleum. C. E. Zobell in his report of this project mentioned that conversion is genuinely a micro-biological process.^{7b} Bacteria, as described by Zobell can survive in fact in all critical conditions, from 0° to 85°C, under extreme pressures upto 10,000 kg/cm² and also at well depths of 10,462 metres.¹³

Laboratory tests confirmed that 'Lipoclastic' anaerobes have the capacity to split long chain hydrocarbons to shorter chains.

Evidence in biogeneicity does not differentiate between vege-

table and animal source.⁵ Close association of crude oil with marine remains suggests that it is from fish molluscs, lamelli-branches, diatoms foraminiferae and other sea creatures, known from their fossilised remains to have been present in immense quantities in ancient seas. Preponderance of petroleum known today is derived from ancient biological matter, particularly from lipid rich lower marine plants such as plankton^{21a}. Terrestrial plants supply terpenes, which suggests the phenomenon of atmospheric volatilisation of vegetation. The nature of recent hydrocarbons found, does however support the biogenic origin; the main reason being the presence of odd carbon number. These matters are often referred as kerogens or mother substances for shale.

According to Kenneth Kobe, petroleum results from a series of biochemical and chemical reactions which start with organic remains of dead micro organisms.⁶ Bacteria are involved in first transformation of the constituents of decaying micro-organisms into hydrocarbons.

Anerobic conditions keep porphyrins to remain in crude; if oxygen had been there these would have been decomposed.⁸ Bacteria can also decompose organic matter to CO_2 , H_2S , etc. Further, it is discovered that no bacteria can produce more than C_2 -compounds, thus C_{11} to C_{14} compounds must have been formed from marine life as is evident from certain Gambian crudes.⁹ Most organisms are found to generate petroleum in their metabolic processes too (Meyer and Hocott).

Crude oils found in the younger sedimentary deposits do in fact contain appreciable amounts of oxygen and nitrogen. This shows organic material as the source. McNab et al divided crudes into three types depending upon the time of deposit¹⁰

Tertiary crudes	: $11 \times 10^6 - 74 \times 10^6$ years of age	
(Eocene oil)		(asphaltic crudes)
Mesozoicera oil	: $75 \times 10^6 - 200 \times 10^6$ years of age	
Paleozoic crudes	: $200 \times 10^6 - 500 \times 10^6$ years of age	
		(Parrafinic Crudes)

Brooks and Frost concluded that the organic matter can be decomposed easily under the action of natural catalyst as well as bacteria.¹¹ The evidence of bacteria in sedimentary

rocks is positive and the organics are initially decomposed to acids and gases (CH_4), till the activity of bacteria ceases due to frankensteinism. I. M. Gubkin demonstrated that the formation of petroleum and gas from organics, scattered in argillaceous rocks was a local process and started really with accumulation of organic matter in sea oozes, be it the fats or carbohydrates. Apart from this, some scientists regard that the hydrogenation of carbon oxides results in $\text{-CH}_2\text{-}$ chains, which may be congenially taking place under the catalytic activity of earth's crust under favourable conditions of temperature and pressure. But this is only a derived literature thrust to explain and can never match with the quantum of oil. Thus every new thought merely results in more sterile addendum. The overall explanation hitherto may be summed up in two steps: firstly the action of bacteria in contributing the lighter fractions, secondly continuous catalytic action of earth at depths of 1-2 Km to yield heavier hydrocarbons. It is observed with the depth of mine and time of formation and storage, the API gravity of crude and paraffinity increase because of severity of reactions, which is in full agreement with the above picture.^{21-b}

These are all possible natural reactions occurring over the ages, and petroleum hydrocarbons might have been formed by many processes and each contributing its own share, may be small.

In conclusion, regarding the biologic origin of petroleum there need not be any doubt, because of the oil association with sediments containing a relatively large amount of organic matter, the presence of optically active compounds and complex substances of obvious biological origin. Oil is also absent from formations having adequate traps and porous strata, but without any organic material. The formation is at low temperature, usually less than 200°C or even 100°C . The thermophilic bacteria (bacteria that can survive at high temperature) plays the major role in conversion of this organic mass into liquid hydrocarbons.

1.2 Reserves and Deposits of World :

There are very few parts of the world which are self sufficient in energy. USSR and Eastern Europe are largely self

sufficient in energy and they never look for outside supplies of oil. Middle East, Africa, the major oil producers are exporters of huge energy, while Japan is a leading importer of energy. U.S.A. is also energy producing country, but its commitments have grown to such an extent, that it is now a major importer of energy.

Petroleum deposits mainly occur in some elevated sections of porous sandy strata.^{1b} Sedimentary rocks accumulate in sea bed at a very slow rate. These layers over millions of years stratify under pressure and temperature and are transformed into metamorphic rocks, sand stones, marbles, etc. These are the basic reservoirs of gas and oil. Whenever fissures and dislocations in zones of earth occur, oil and gas reach surface and get burnt continuously by accidental fires like lightning, etc. and sometimes oil drains to nearby streams too. A false understanding prevails that volcanic eruptions are followed by huge quantities of hydrocarbons.

It is seen coal is more uniformly distributed throughout the world rather than oil; oil is scattered randomly and 80% of oil found to date occurs in what has been called oil-axis-pole.^{4(b)} Gulf Carribbean, Mesopotamian and Persian Gulf are such areas confined to depressions on earth's crest. Initial migration of oil takes place during compaction of dense shales.¹² Although the migration mechanism is not fully understood, evidently it is not effective, with the result, much oil is left in the formations. At present oil from such source is not economically recoverable.

Bacteria in marine sediments may also contribute to the liberation of oil from oil bearing materials in various ways. According to Stone and Zobell obvious import is the bacterial decomposition of organic complex in which oil is trapped.¹⁸ Secondly by dissolving carbonates or sulfates on which oil is absorbed by action of bacterial acids. Thirdly bacterial gases reduce the viscosity of oil.

In Soviet Union, the South Caspein Basin, Ural-Volga Basin, and Western Siberian Basins are famous for hydrocarbon deposits which rank next only to Irano-Arabian Basin, the richest in the world.

Once the richest basin, Aspheron-Peninsula has been exploited since last hundred years. An idea can be had through

approximate records that oil extracted throughout the world till 1975 is about 43,000 MMT, a considerable amount of which was produced during 70's only.

Kuwait, a small country with 18% of world reserves held its 4th position for a long time in the production of oil after U.S.A., U.S.S.R. and Venezuela, but now Iran and Saudi Arabia have, surpassed Kuwait. Saudi Arabia is about 100 times bigger than Kuwait and is ranking next to Iran with 10MMbbls. per day. Kuwait is producing approximately 1.25MMbbls. per day.

U.S. crudes are relatively less sulfur ones and make up about 7% of world reserves.¹¹ Venezuela and African crudes of relatively low sulfur content constitute about 10% world oil reserves. African countries like Libya, Algeria and Nigeria account to about 300 million tones per annum. A characteristic feature of the oil wells near Middle East is high yields per well. Iraq and Iran are famous for such types of wells, which can produce even 10,000-20,000 tons per day per well. Thus near and Middle East countries with highest proven reserves of 70% of world's petroleum stock holds the control in the energy export.

At present the trade is governed by OPEC*; fortythree percent of world crude produced in 1972 was shared among the group members, which is very much true today also.

1.2.1 WORLD RESERVES

Several estimates of world hydrocarbon reserves were made by almost all leading institutions and companies. As furnished by Weeks the estimates of proven reserves are $1,900 \times 10^9$ bbls of oil against the estimates of Warman (British Petroleum Company) 1,200 to $2,000 \times 10^9$ bbls. There is no congruency of expression in these reserves; one can judge by the following ultimate reserves as presented by Richard G. Sieidl^{1b}, how the estimates once cited regularly change with better methods of surveys and techniques.

* OPEC : Organisation of Petroleum Exporting Countries A 13 Member body consists of :

(1) Algeria, (2) Iran, (3) Iraq, (4) Saudi Arabia, (5) Gabon, (6) Kuwait, (7) Ecuador, (8) Libya, (9) Indonesia, (10) Nigeria, (11) Qatar, (12) United Arab Emirates, (13) Venezuela.

1965	Hendricks	$2,480 \times 10^9$ bbls
1968	Shell Company	$1,800 \times 10^9$ „
1970	Moody	$1,800 \times 10^9$ „
1971	U.S. National Petroleum Council	$2,670 \times 10^9$ „
1972	Weeks (8th WPC, Proceedings 2, P 99-106)	$3,650 \times 10^9$ „
1975	Whiting (recover- (Jan. 1st) able)	556.2×10^9 bbls and 80×10^{12} cu.M. gas.
1977	Harry Warmen ¹⁶ (Jan. 1st) (recoverable oil reserves)	270×10^9 Tons of oil Gas equivalent to 55×10^9 ton of oil

Total proven reserves as per Whiting goes upto $2,2000 \times 10^9$ bbls of oil and 250×10^{12} Cu.M. of gas ; of which 30% will be a offshore product and rest onshore. Cumulative oil production of world till January 1974, was put around 270×10^9 bbl oil and 20×10^{12} Cu.M. of gas.¹⁵

Next to coal, natural gas reserves of 60 billion tons oil equivalent are highest in the world ; with a proven to potential capacity of 30% for gas and 60% for oil, the chance of finding more amount of gas is always bright.³²

John J. McKetta³⁸ et al have presented the following data on the available energy of today (1980) and estimates of reserves of energy sources :

Available energy today :

Fossil Fuels

Oil	570×10^9 bbls
Natural gas	2,500 Exajoules
Coal	637×10^9
Shale	30 gigatons
Tar sands	15.30 gigatons
Nuclear Source	310 MW

Renewable Energy	
Geothermal	132 MW
Hydroelectric	5.7 Exajoules
Solar	negligible
World oil estimates	240-260 gigatons
Natural gas	10,500 Exajoules
Of which undiscovered	8,150 Exajoules
Coal	10,125 billion tons
Of which known reserves	637 billion tons

Nuclear

Uranium	3 Million tons
Thorium	630 Thousand tons
Additional undiscovered Uranium	80-280 Million tons
Exajoule	= 160 Million barrels
Gigaton	= Billion barrels

At present the production of oil in the world is about 2300 MMta and gas over one trillion cubic meters, and is expected to reach a maximum production of 2700-2800 MMta of oil during this decade and likely to witness a drop in production by the end of this century to a quantity 2000 MMta. A further drop is likely by 2050 AD to about 1500 MMta. Long range predictions are unwarranted, due to the volatile political situations and war clouds hanging on every part of the world. Perhaps time may not be kind enough to permit man to utilise the last tonne of oil due to man's cupidity and insecurity prevailing on every part of the globe.

Fears of impending oil shortage have raised hopes of finding huge deposits of oil even under deep oceans. The activity now-a-days is more confined to such areas.

According to Klemme there are 334 giant fields in 66 basins that contains 70-75% of oil. Indian subcontinent is placed in Type 4 basin (India and Assam) and the costal belt in pulled apart basins.

Estimated sedimentary rocks of the world, by D. Ion and Hendricks is about 62×10^{17} tons, which contain an organic

matter of 3.5×10^{15} tons, which in turn can yield a hydrocarbon content of 7.7×10^{13} tons.¹⁷

1.3 Indian Petroleum Industry

The world's petroleum industry dates back to first refinery of 5 bbl capacity at Pittsburg, started by Samuel Kier in 1855. Incidentally the first oil well was dug by Drake in August 1859 at Titusville. Indian oil industry was not lagging very much at its inception, as the first oil well was dug in 1866 and the first refinery started in 1893. Assam Oil Company's refinery at Digboi was the only major refinery till 1954. People were under firm impression that there was no possibility of finding oil resources in India. International Oil Companies as a group had written off India, as a barren land where there was no possibility of oil being found, except in parts of Assam. The Government of India when it started the refineries on sea coasts it was based on the hope of getting oil from international market. Providence helped India to invite the Russian experts; accordingly in 1955, a team of top geologists and oil experts arrived. Discreet surveys made by the team showed promising areas. In a short time, the discovery of Cambay oil field (1958) followed by Ankaleswar, strengthened hopes and launched the collaboration between USSR and India, exposing all the designs of multinationals. With the Russian team under the leadership of Prof. Markevitch still assisting, there is every chance of putting India on to the world oil map.

The birth of ONGC, discovery of new oil fields in eastern and western parts of country, had laid the major path for the country's progress on the oil front.

Recent remarks of Dr. R. Santoro, leader of Italian delegation shows that India shall emerge as a major oil producing country in 10 years.

Since 1949 to 1960 Standard Vacuum Oil Company alone explored the West Bengal basin and later jointly with Government of India. Till a year back, the major crude producing concerns in India were Oil India Limited, Oil and Natural Gas Commission and Assam Oil Company. Now all private sector industries are taken over by the Government.

Real foundation of oil Industry in India took place during

the second Five Year plan (1956-61) when the Government of India launched a planned programme of exploration, production refining and distribution of oil. Accordingly ONGC took birth in August 1956 with assigned duties of exploration and production of oil, on-shore as well as offshore. Next to come into oil field was Oil India Limited a joint venture of Government of India and Burmah Oil Company (1956), which was given lease to explore and produce oil in North-Eastern parts of India.

Indian Oil Corporation Ltd. floated in 1958 had come into existence with the objectives of procuring, processing of oil and distribution. It has been divided into two wings as Refinery Wing and Marketing Division. The Refinery Wing takes care of procurement, processing and installing of new refineries, while the Marketing division takes all necessary steps to distribute the products to every corner of the country and export certain products.

Compared to developed countries, like USA, where 30% of reserves were already consumed, the developing countries, particularly India has a bright future. The maximum reserves of the country are put around 2462 million tonnes of oil and gas at 843×10^9 cubic meters by ONGC. The discovery of Bombay High (1973) and Bassein area had brought a great relief to the Government. According to offshore project Director of Bombay High, Dr. Prasad the conservative estimates of oil is around 700 MMt in Bombay High alone.¹⁸ This basin is a small part of approximately 140,000 sq. Kms. of the vast sea coast of India running about 6000 Km. By 1982, Bombay High alone shall be able to produce 12 MMta. High quality associated gas accompanying this oil shall be about 4×10^6 cu. meters per day. Perseverance of quest by ONGC has resulted in the discovery of oil deposits in another propitious delta region, Godavari basin and gas fields in Andamans, the estimates of which may surprise every one. The Mahanadi and delta areas of West Bengal are still in the process of exploration; it is likely, as is evident from the report submitted to the United Nations Industrial Development Organisation (UNIDO) that the sedimentary deposits of Bay of Bengal are unique in 20 Km. thick in comparison to 16 Km. thick deposits of USA and these basins may yield unexpected quantities of oil. With Indian sedimentary region

covering more than a million square kilometers, it may be possible to extract 4 billion tons of oil and 2 trillion cubic meters of gas without even counting reserves of continental shelf. The present estimates in the offshore areas (Bombay High alone) is put around 2.5 billion tons.

Oil India Ltd. till now is credited with a production of 50 MMt. Further, it has undertaken to a more systematic and thorough exploration of sedimentary basins of Mahanadi and Bengal and other North-Eastern regions ; with these active plans, Oil India has formulated an ambitious plan to produce 60 MMta of crude by 2000 A.D.

With recent finds of oil in Arunachal and Paradip area, Oil India Ltd. is thinking of setting up a small refinery in Arunachal Pradesh to meet the demands of that area.

India's offshore continental slope of 400,000 sq. kms and another 400,000 sq. km. continental shelf, with approximately one million sq. kms. of sedimentary area on land, offer intelligibly a bright future and prospects to the oil industry.¹⁹

India's offshore basins are expected to yield one billion tons of oil and 4 billion tons of gas ; the offshore basins are listed below²¹ :

Kutch	28,000 sq. kms.
Saurashtra	32,000 „
Godavari	32,760 „
Mahanadi	12,040 „
Bengal	28,280 „
Cauvery	26,320 „
Andamans	3,500 „
Kerala	81,480 „
Bombay High	1,40,000 „

With the vigorous activities on the oil front a production of 16 MMt. during 1981-82 is conceivable ; however a gap of 15-16 MMt of oil as products has to be bridged by imports.²⁰

Crude production from ONGC wells will be stepped up from anticipated level of 13.21 million tons this year to 17.51 millions during 1982-83. Cooking gas production is also proposed to be raised from about 75,000 cubic meters this year to 1.41 lakh cubic meters next year. Bulk of the increased oil production in

the country during next few years will come from Bombay Offshore areas.

ONGC is planning to increase marginally crude production from present figure of 5.31 million tonnes to 5.41 million tonnes, during next year. In view of Bombay High production some of the wells in Gujarat may be plugged.

It may be a paradoxical picture to mention, that per capita reserves of oil, in India are 1/6th that of China or 1/20th of USA, while coal reserves (176 tonnes per capita) are not at all comparable with the above mentioned countries. This definitely proves wrong those who think that coal reserves in the country are the answer to energy problems.

The contemplations of Government to reach a target of 100 MMta by next 20 years, if achieved will perhaps make the country self sufficient in oil production. With the set land mark of 10 MMta from Bombay High, already achieved very recently (1981) the indigenous production has shot upto 16.5 MMta ; this necessitates a reduction of 1.5 MMta in crude imports in the coming year (1982-83).

Crude would be imported into India from various sources during 1982 is like this

Iraq	— 3.5 MMt	(additional 1.5 MMt over the existing contract)
Venezuela	— 0.5	„
Nigeria	— 0.5	„
Iran	— 9.8	„
U S S R	— 2.5	„
Abudhabi	— 1.0	„
Saudi Arabia	2.5	„

Other countries that supplied crude to India during the last few years

Indonesia	— 1.2 MMt/year
Mexico	— 1.5 „
Kuwait	— 1.0 MMt (products)
U S S R	— 0.5-1.0 MMt, products

The present output of refineries is about 30 MMta, with Mathura refinery already on trial runs. By the end of this decade

the refining target of 40 MMta shall be achieved without any doubts.

Some of the statistics on petroleum production and consumption are presented at the end of this chapter. The refining pattern of Indian refineries is also added to benefit the readers.

The oil map of India (Fig. 1.1) shows the vast capabilities of our country in the offshore and onshore prospective areas.

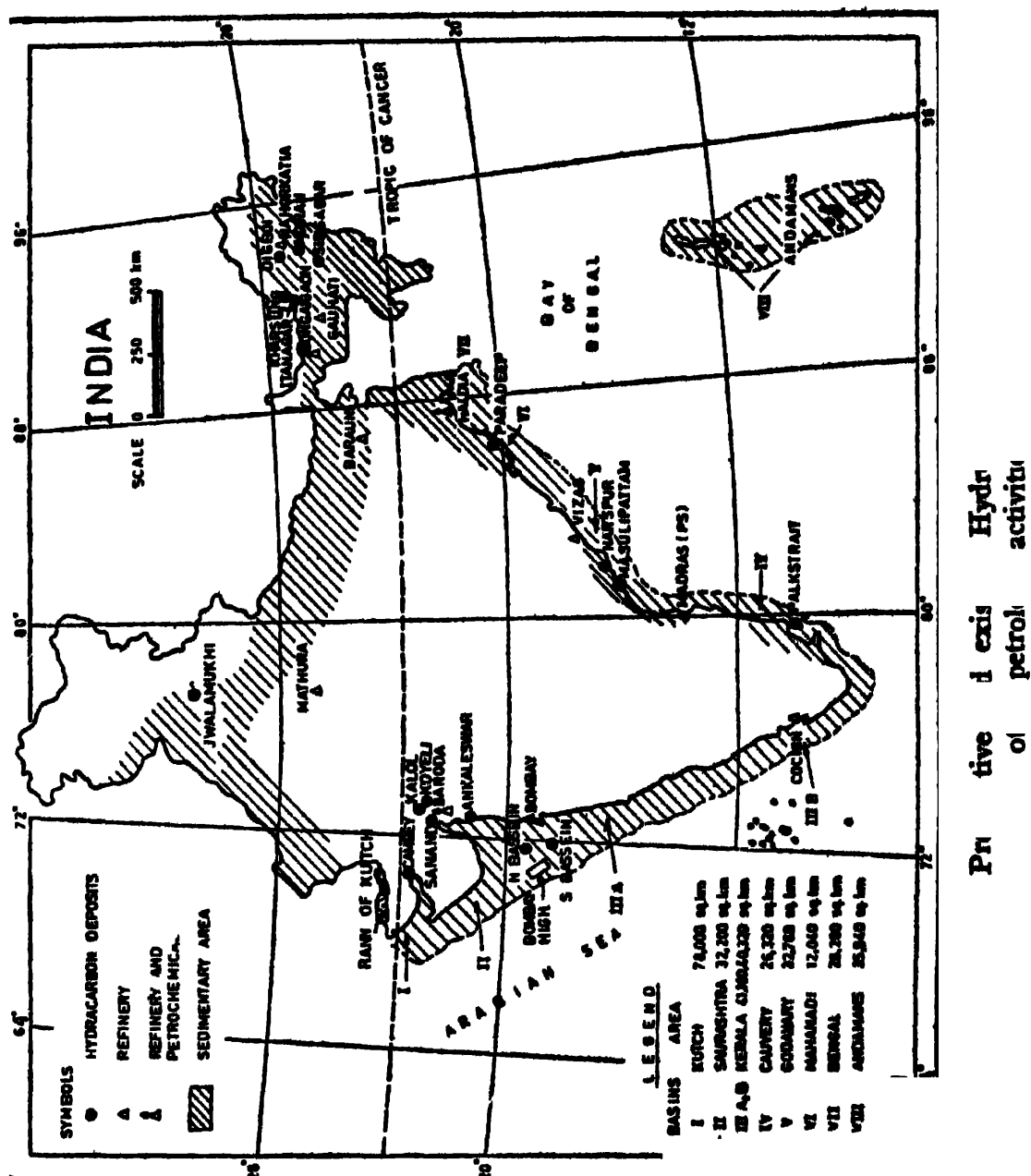
1.4 Composition of Petroleum

Petroleum occurs in nature in all three possible states solid, liquid and gas. The liquid petroleum is usually coloured from dark brown to bluish black or black, exhibiting some times bloom or fluorescence. The semi-solid or solid petroleum is well known by the name pitch, usually black in colour. The famous pitch lake of Trinidad is an example of such vast deposits of petroleum in solid state. Such kind of deposits are assumed to form after the evaporation or migration of lighter fractions. The gaseous deposits of petroleum are known as natural gas deposits, where sometimes wild gasolines are also accompanied. Gas from condensate reservoirs contain a good portion of lighter fractions of a boiling point upto 30° C. Associated reservoirs contain gas mainly in dissolved form in liquid petroleum.

Although the composition of petroleum depends not very much on the origin of formation, but certainly change with the time of formation, storage and different stratas through which it migrated. It is a homogeneous mixture of various hydrocarbons of saturates and ring-structures. The average ultimate composition of petroleum is mainly given in terms of constituents of hydrocarbons, namely carbon and hydrogen as follows :

Carbon	: 84—86%
Hydrogen	: 11—14%

The other major elements of importance are sulfur, oxygen and nitrogen. These elements in hydrocarbons are usually treated as impurities because of their inherent properties like odour, colour corrosiveness etc. Generally these three elements combined do not exceed 5% on an average. Exception to this statement can be traced in some Gulf crudes, Russian crudes and



Pn tive d exis Hydr
of petrol activitu

Mexican crudes. Ratwi (Neutral zone) contain as much as 5% of sulfur alone. Middle East and Gulf crudes contain upto 3%, compared to these, crudes from East possess very less amount of sulfur, examples being Indonesian, Indian, Nigerian, and Libyan crudes.²² The crudes of U.K., like Beryl, contain upto 0.5% sulfur.

The bulk of petroleum is made up of hydrocarbons of saturated compounds like paraffins, naphthenes and unsaturated cyclic compounds mainly aromatics

The highest carbon atom present in the crude is C_{70} . Further, except first few hydrocarbons, all other hydrocarbons exhibit isomerism. The general properties of these homologous series are discussed below :

1.4.1 PARAFFINS

C_nH_{2n+2} is the general formula of paraffins. First three compounds are gases while compounds upto C_{16} are liquids and beyond that, they assume semisolid consistency. Well beyond C_{30} assume shape of solid blocks, sometimes even crystalline forms. There are number of isomeric compounds for each compound, profoundly differing in properties. For example, upto C_3 no isomers are possible, C_4 exhibits only two isomers, as shown here :



And C_5 exhibits three isomers. The number of isomers increases as the number of carbon atoms increase. $C_{15}H_{32}$ exhibits 802 isomeric forms.

1.4.1.1 General properties of paraffins

Paraffins are stable, not attacked by sulphuric acid or other oxidising agents. However, paraffins of higher order $> C_{30}$ are prone to oxidation. Even usual oxidising agents like potassium permanganate can cause good amount of oxidation. The aptitude to contribute the substituted products with halogens has magnified the petrochemical industry. Higher paraffins are very

much insoluble in water ; though the lower ones are soluble in ethers and alcohols. (Fig. 1.2)

Paraffins upto 3 carbon atoms have inclination to form hydrates such as $\text{CH}_4 \cdot 7\text{H}_2\text{O}$, $\text{C}_2\text{H}_6 \cdot 7\text{H}_2\text{O}$ and these hydrates offer clogging and corrosion difficulties. Hence drying is essential before usage.

The specific gravity of the series increases with molecular weight, still paraffins have less specific gravity and boiling point than aromatics. Viscosity of paraffins is less but viscosity index is high in contrast to aromatics. The smoke point of the paraffins is very high, with poor illuminating characteristics. The pour point of paraffins is usually high ; due to this paraffin rich crudes and products bring difficulties in transporation and storage.

Isomers differ from *n*-paraffins by having slightly low boiling points, low pour points, high viscosity and viscosity index. Usually *i*-paraffins, are more reactive than *n*-paraffins but burn like *n*-paraffins without much illumination and smoking.

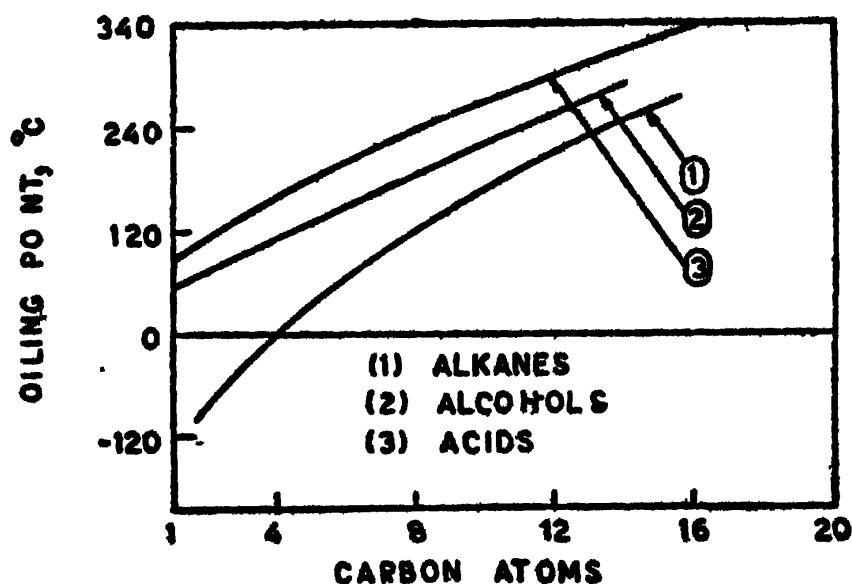


FIG 12 Boiling points of first few alkanes alcohol and acids

High molecular compounds ($> \text{C}_{20}$) may be of saturated or unsaturated nature, decompose if exposed to a temperature of above 370°C . Vacuum distillation is essential for distilling such boiling stocks to prevent them from thermal degradation.

1.4.2 UNSATURATES (Olefins and Properties)

Olefins are represented by the general formula C_nH_{2n} . The first four are gases and upto C_{16} are liquids and beyond C_{16} are solids. The boiling points of olefins are generally lower by few degrees than the saturated compounds of the same carbon number. Chemically these differ very much from paraffins. They are easily attacked by sulfuric acid and some of them even polymerize. Treatment with sulfuric acid and subsequent hydrolysis yields alcohols (e.g. isopropyl alcohol) and with permagnate oxidation, glycols are formed. Unsaturated compounds like olefins, diolefins, in general, do not appear in crudes to measurable quantities, however they are detected in some crudes. These unsaturates are mainly formed during cracking operations. The absence of unsaturates to a large extent can be best judged by the probable catalytic activity of the earth's crust in converting unsaturates to saturates and ring structures.

1.4.3 ACETYLENES AND PROPERTIES (ALKYNES)

The general formula for this series is C_nH_{2n-2} . These are isomeric with diolefins. Acetylenes yield crystalline compounds with ammoniacal solution of copper salts and are attacked by sulfuric acid. Acetylenes can be readily hydrogenated to give stable compounds.

1.4.4 DIOLEFINS

These are represented by the formula C_nH_{2n-2} . Like other unsaturates, these are produced during cracking reactions. These can be distinguished from acetylenes as they do not form salts with ammoniacal solutions of copper salts. But with mercuric chloride these form precipitates and sulfuric acid polymerises these unsaturates.

1.4.5 NAPHTHENES

These are saturated ring compounds bearing the general formula C_nH_{2n} . The prominence of ring structure starts with five carbon atoms. Although C_3 and C_4 ring structures,²⁸ are in existence, their stability is decreased because of excessive strain (Bayer's Strain Theory). Naphthenes are isomeric with olefins but differ profoundly in properties. Naphthenes exhibit both the

properties of saturated paraffins and unsaturated aromatics, the result of which, all the properties like sp. gravity, viscosity, pour point, thermal characteristics lie in between the two mentioned homologues. Usually, all the ring structures are having branched chains, where the isomeric character predominantly occurs, followed by positional isomerism in rings (Fig. 1.3).

1.4.6 AROMATICS

The first and smallest of the aromatics is benzene; other simple aromatics to follow are toluene, xylene, cumene etc. Even though benzene is unsaturated, yet it follows the principles of substitution with halogens rather than addition. This is mainly due to symmetric grouping of closed ring structure and resonance.

Aromatics are usually having high boiling points, low pour points (freezing points), high octane numbers, high viscosity and low viscosity index and these burn characteristically with a red flame with much soot. As these behave like saturates, they resist oxidation. In petroleum fractions aromatics beyond 3-ring structure (Anthracenes) are probably non-existent. Aromatics usually extend their presence from a temperature of 80° C onwards and well dominate in lower middle cuts and heavy cuts. Actually the light aromatics (BTX) do not exceed even 5% of crudes of general nature. Bulk of the aromatics are with side chains and naphthenes and exist in heavier portion of crudes.

1.4.7 INORGANICS

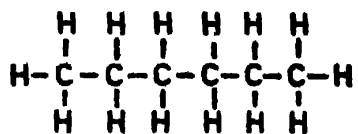
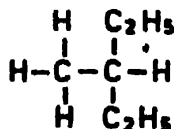
Sulfur compounds : Sulfur is found in most of the crudes in variable amounts. Generally sulfur compounds are present in more quantities in higher molecular weight stocks. Usually the sulfur content does not exceed 5%, however rare exemptions are : Venezuela (5.25%), California (USA 5.21%), Qaiyarah (Iraq—7%) etc. crudes.

Sulfur in crude occurs in different forms like free sulfur, hydrogen sulfide, mercaptans and thiophenes etc. These are frequently occurring compounds in almost all fractions of the crude though to a different degree. Heavier fractions contain sulfides, polysulfides, sulphonates and sulphates.

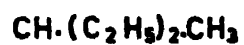
Sulfur occupies prominent position in refining due to its ominous problems of corrosion and odour. Pollution problems

ALKANES (C_nH_{2n+2})

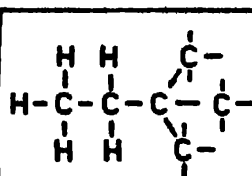
n - HEXANE

ISOMERS of C_6 

Methyl diethyl methane



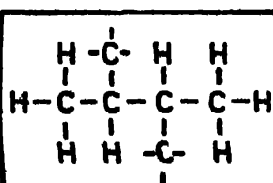
2, Ethyl butane



Tri methyl propane



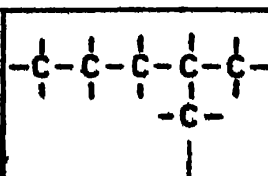
2,2 Dimethyl butane



Dimethyl butane



2, 3 Dimethyl butane



Methyl pentane



2, Methyl pentane

FIG. 1.3 Structures of some organic compounds

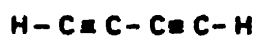
OLEFIN (TERPENS) C_nH_{2n-4}

Triolefins	C_nH_{2n-6}
Di-acetylenes	C_nH_{2n-6}

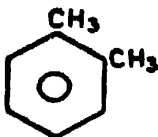
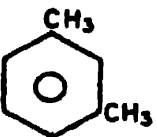
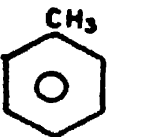
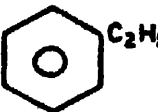
AROMATICS

Benzene series	C_nH_{2n-6}
Nephthalene series	$C_{10}H_8$

Diacetylenes



ISOMERISM IN AROMATICS

 1,2,4-Xylene	 1,3 m-xylene	 p-xylene	 Ethyl Benzene
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Mesitylene C_9H_{12}

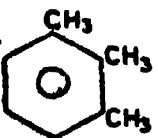
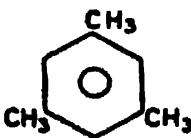
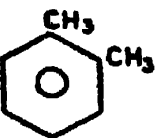
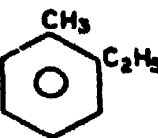
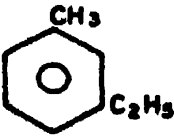
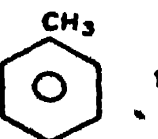
 Trimethyl benzene	 Mesitylene	 Cumene	 1,2 Ethyl Toluene
 1,3 Ethyl Toluene		 1,4 Ethyl Toluene	

FIG. 1.3 (Cont.)

OLEFINS ($C_n H_{2n}$)

$C = C - C - C$	α - Butylene
$C - C = C - C$	β - Butylene
$ \begin{array}{c} C - C = C \\ \\ C \end{array} $	γ - Butylene (iso-butylene)

CYCLO - PARAFFINS ($C_n H_{2n}$)

	Cyclo - hexane
	Cyclo - butane
	Cyclo - pentane

DI-OLEFINS ($C_n H_{2n-2}$)

$CH_2 = C = CH_2$	Allene
$CH_2 = CH \cdot CH = CH_2$	Divinyl (butadiene)
$CH_2 = CH \cdot C \cdot CH = CH_2$	Isoprene (2 methyl , 1,4 divinyl)
$CH_2 = C \cdot C = CH \cdot CH_3$	Piperlene

ACETYLENE ($C_n H_{2n-2}$)- $C \equiv C$

$HC \equiv C - CH_3$	Methyl acetylene or Propyne-1 or Alkyne
$CH_3 - C \equiv C - CH_3$	Crotonylene or Butylene-2
$C_2 H_5 - C \equiv C - CH_3$	Ethyl methyl acetylene or Pentyne-2

FIG. 1.3 (Cont.)

SULPHUR COMPOUNDS

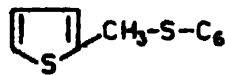
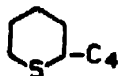
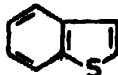
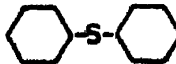
Mercaptans	$C_n H_{n+1} SH$	
	$C_2 H_5 SH$	Ethyl mercaptan
Sulphones	RSO_2	
	$C_7 H_{15} SO_2$	Heptyl Sulphone
Sulphides	$R_2 S$	
	$(CH_3)_2 S$	Dimethyl sulphide
Di Sulphides	$R_2 S_2$	
	$CH_3 S S CH_3$	Dimethyl disulphide
Sulfoxides	$\begin{array}{c} R \\ \diagup \\ SO \\ \diagdown \\ R \end{array}$	
	$\begin{array}{c} CH_3 \\ \diagup \\ SO \\ \diagdown \\ CH_3 \end{array}$	Dimethyl sulfoxide
Thiophenes		
	 CH_3-S-C_6	Thiadecyl thiophene
Thiophanes	$C_n H_{2n} S$	
	 $-C_4$	Butyl thiacyclohexane
Sulphates	$(C_n H_{2n+1}) SO_4$ $R_2 SO_4$	
		Thio benzols
Sulphonates	 SO_3 $R SO_3$	
Carbonyl Sulphide	$C O S$	
		Cyclopentyl-cyclohexyl sulphide
	 $-C$	Thio cyclo heptane

FIG 1.3 (Cont.)

NITROGEN COMPOUNDS

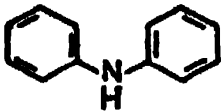
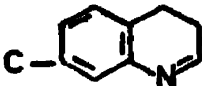
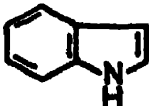
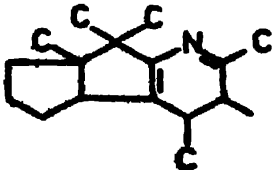
Carbazole	
Pyrole	
Methyl Quinoline	
Indoles	
Quinoline	$C_9 H_7 N$ $C_{12} H_{17} N$ $C_{13} H_{18} N$ $C_{14} H_{19} N$ $C_{15} H_{19} N$
Pyridine	
Pyrroles	

FIG. 1.3 (Cont.)

OXYGEN (Naphthenic Acids) compounds



$C_6 H_{11} COOH$	Hepta naphthenic
$C_7 H_{13} COOH$	Octa naphthenic
	Furan
	Benzo Furan

Porphyrins

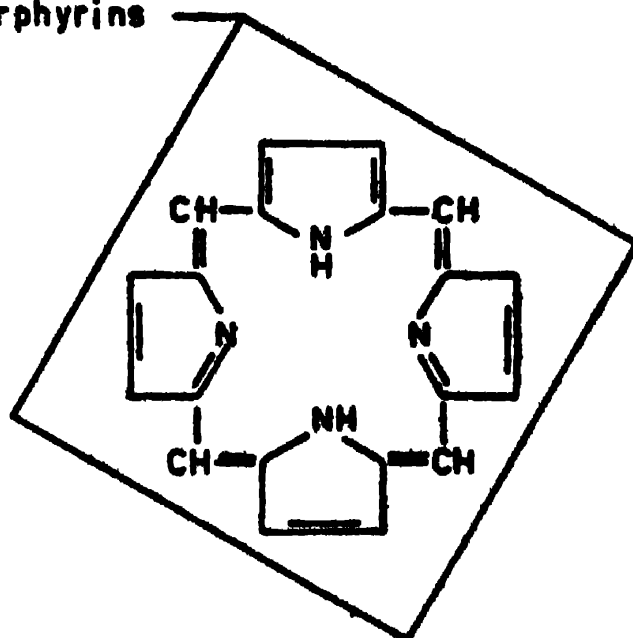


FIG. 1.3 (Cont.)

and following cost of waste treatment is punitive for all refiners with high sulfur-stocks. However, refiners habitually remove more detrimental sulfur compounds and leave the less harmful ones into the products, as seen in the case of sulfides converted to disulfides in gasolines. Some of the sulphonates are regarded as good emulsifiers and detergents, hence promptly extracted for use in cutting oils. Conspicuous effect of sulfur is reflected in increasing the density of crude.

A correlation presented by Obolentsev²⁵ shows the influence of sulfur on gravity

$$\rho_{\text{at } 20^{\circ}} = 0.0087 (S\%)^2 + 0.0607 (S\%) + 0.7857$$

Different crudes are presented in Table 1.1. It clearly shows the effect of sulfur on API gravity of crude and pour point of crude. All sulfur crudes mysteriously exhibit low pour points.

Further, sulfur containing residuums when cracked leaves cross linked structures, resembling the phenomenon of vulcanization of rubber and offer perennial problems in desulfurisation. Its presence in different fractions complicates the refining and treatment methods. Yet another problem is, it desists the effects of additives. Sulfur in gasoline inevitably depresses the effect of lead and demands more amount of additive. When crude contains more than 0.5% S, it is denoted as high sulfur crude. A terse distinction, at this juncture between sour crudes and sulfur crudes is desirable. Free hydrogen sulfide is available in some crudes, which naturally fosters corrosion. Such crudes are classified as sour crudes; other sulfur bearing compounds are not taken into this account. The crudes containing sulfur compounds other than hydrogen sulfide and exceeding 0.5 % are denoted as high sulfur crudes.

1.4.8 OXYGEN AND NITROGEN

Oxygen and nitrogen do not occur in free state either in crudes or in fractions. Nitrogen presence in free form is well known in natural gas only. Oxygen occurs as oxygenated compounds like phenols, cresols, naphthenic acids, sulphonates, sulphates and sulfoxides.

Nitrogen exists in the form of indoles, pyridines, quinolines

TABLE 1.1
EFFECT OF SULFUR ON GRAVITY AND POUR POINT.²⁶

Crude	A P I	Pour Point °C	Sulfur %
Cyrus (Iran)	19.0	—23.3	3.48
Iranian Heavy	30.8	—20.6	1.6
Kuwait	31.2	—17.8	2.50
North Slope (USA)	26.8	—20.6	1.04
Qatar Marine (Qatar)	37.0	— 3.9	1.50
Romashkinskaya (USSR)	32.6	—28.9	1.61
Bassein (India)	38.45	+30	0.15
Nahorkatiya	31.0	+30	0.16
Ankleshwar	47.0	+15	0.05
Bombay High	38.0	+30	very low
Arabian (Light) (S. Arabia)	33.4	—34.4	1.80
Arabian (Heavy) (S. Arabia)	28.2	—34.4	2.84
Arjuna (Indonesia)	37.7	+26.7	0.12
Bu Attifel (Libya)	40.6	+39.0	0.10
Basrah (Iraq)	33.9	+15.0	2.05
Brass (Nigeria)	43.0	—20.6	0.08
Darius (Iran)	33.9	—17.9	2.45

and amines, usually well below 2%. Nitrogen compounds exasperate problems in processing and stability of products. Catalyst deactivation or poisoning, gum formation are some of the offshoots of nitrogen. Nitrogen is present in two forms, basic and non-basic. Basic²⁴ nitrogen is characterised by its titratability with perchloric acids, whereas nonbasic nitrogen is not titratable hence no possibility of extraction. Most of the nitrogen²⁷ pigments impart color to crude and fractions. The most interesting compounds of nitrogen are porphyrins. These are obtained from living organisms and preserved in petroleum. It stands to reason that aneorobic conditions were prevailing during petroleum formation; otherwise oxidation would have

destroyed them. Chlorophyll²⁸ is also a complex of porphyrin, where central atom is magnesium instead of nickel or vanadium or iron. Iron porphyrins are also known as heme, the constituents of red cell in the blood.

Porphyrin^{29, 34} pigments are usually associated in complex form with metals like, copper, iron, vanadium and nickel. The proper understanding of these pigments³⁰ may augment the knowledge of origin and formation of petroleum. The following is an example of nitrogen complex .

Gravity API	— 38.8
Sulfur wt. %	— 0.2—0.0%
Vanadium ppm.	— 0.5—2.5
Nickel ppm.	— 1.0—170
Vanadyl porphyrin ppm.	0.7—1130
Nickel porphyrin ppm.	1.0—390

1.4.9 ASPHALTS, RESINS AND BITUMENS

Asphalts are high molecular weight complex molecules, black in color, soluble preferably in aromatic solvents and carbon disulphide. Resins are mostly compounds of highly condensed ring structures, containing oxygen, sulfur and nitrogen, sometimes inorganics too. Though bitumen is a manufactured product, it is essentially made up of three components, asphalts, resins and mineral oil. These three components comprise a colloidal system ; asphalts are suspended in oil and resins contribute to the stability of the system.

1.4.10 LESS INORGANICS

The other elements present are nickel, vanadium, iron, silica, sodium, magnesium, and halogens etc. Even though the analysis is not desirable as these metals hardly exceed 0.01%, yet may be analysed for sensitive purposes. The ash formation is mainly due to these metals and inorganics. Sometimes organometallic compounds are available in colloidal form. Inorganics always leave a marked influence on fractions, for example halides may give off halogens during hydrolysis or thermal decomposition. Corrosion, pollution, ash etc. are mainly contributed by inorganics and the quality of crude and fractions are always debased by these small amounts.

Table 1.2 (a) shows some statistics on completed Oil Wells during 1975 in the world.

Table 1.2 (b) shows the World Primary Energy Consumption during 1975.

Table 1.2 (c) shows utilisation of natural gas and oil by different countries.

Indian statistics on Oil and Gas reserves are shown in Table 1.3 (a).

Production statistics of crude oil and natural gas in India since 1960 to 1981 are shown in Table 1.3 (b).

Refining activity of Indian Refineries is shown in Table 1.3 (c).

Different products, produced by Indian refineries is shown in Table 1.3 (d).

Consumption pattern of petroleum products in India is presented in Table 1.3 (e).

Refining capacity of the world and statistics crude and gas reserves and production ; of some countries are presented in Table 1.3 (f) & (g).

Indian Refineries, Crude through put and various units are shown in Tables 1.4 a, b & c.

Table 1.5 shows the milestones in Indian Petroleum Industry

Table 1.6 shows the properties of different crudes processed in India.

TABLE—1.2(a)
WORLD OIL WELL COMPLETIONS DURING 1975

Country	Oil	Gas	Dry	Others	Average Depth Metres
N. America					
(Total)	17,449	9,615	14,404	1,243	1,407
U.S.A.	16,626	7,437	13,203	1,121	1,451
Venezuela	246	6	35	96	1,806
Africa					
(Total)	273	14	332	151	1,852
Algeria	65	10	8	20	2,417
Nigeria	57	—	178	111	1,621
Middle East					
(Total)	409	20	140	191	2,330
Iran	95	11	29	18	2,775
Iraq	36	—	9	—	2,699
Saudi Arabia	101	—	16	95	2,135
Asia (Total)	576	81	358	51	1,691
India	90	6	19	8	2,171
Indonesia	410	38	145	37	1,283
World					
(Total)	20,089	9,995	16,047	1,807	1,472

TABLE—12(b)
WORLD PRIMARY ENERGY CONSUMPTION DURING 1975

Country	Million tonnes oil equivalent					
	Oil	Natural gas	Solid fuels	Water power	Nuclear	Total
U.S.A.	764.2	515.7	342.1	78.4	40.0	1,740.4
Canada	82.5	45.0	16.7	61.7	3.7	209.6
Latin America	173.9	47.7	51.2	33.2	0.5	306.5
U.K.	92.1	32.9	71.5	1.2	6.8	204.5
West Germany	128.6	33.0	70.2	5.4	4.9	242.1
Middle East	70.4	30.0	1.9	1.7	—	104.0
Japan	239.8	7.8	68.6	19.1	5.9	341.2
U.S.S.R.	370.0	233.1	379.0	40.7	5.5	1,028.3
China	55.5	4.7	321.8	6.3	—	388.3
World	2,701.8	1,108.3	1,889.1	373.1	82.7	6,155.0

TABLE—12(c)
UTILISATION OF NATURAL GAS AND OIL BY DIFFERENT COUNTRIES

Country	Utilisation of Natural Gas (10 ⁶ Cu M.) (1974)	Growth of World wide resources (10 ⁸ Barrels) (1977)	Oil produced (10 ⁸ Barrels) (1975)
North America			
U.S.A.	697,673	37,199	3,570,926
Latin America	611,662		
Western Europe	45,938	29,609	1,603,695
Eastern Europe	163,305]	24,539	3,955,917
U.S.S.R.	309,773]		
Middle East	261,000		
Africa	41,934	367,681	7,143,494
Asia	16,617	60,570	1,821,954
India	63,380	19,391]	
China	1,010		1,377,919
	33,980		
World (Total)	1,338,602	640,081	19,473,903

(Source for Tables 1.2(a), (b) & (c) & 1.3a to 1.3c Oil Statistics (1975 & 1976) ; Petroleum Information Service,
New Delhi)

TABLE—1.3(a)
OIL AND GAS RESERVES (INDIA)

Area	1966	1970	1975	1977	1978*	1979*	1980*
1. Crude Oil @ (Million Tonnes)							
On Shore	153.00	127.84	130.13	127.90	125.99	128.15	135.38
Off Shore	—	—	13.77	175.28	221.04	226.29	230.95
Total	153.00	127.84	143.90	303.18	347.03	354.44	366.33
2. Natural Gas @ (Billion Cubic Metres)							
On Shore	63.15	62.48	81.39	80.39	79.71	79.58	80.95
Off Shore	—	—	6.28	148.08	186.15	264.64	270.96
Total	63.15	62.67	87.67	228.47	265.86	344.22	351.91

* As on 1st January of each year.

@ Proved and indicated balance recoverable reserves.

TABLE-1.3(b)
PRODUCTION OF CRUDE OIL AND NATURAL GAS

Company	1960-61	1965-66	1970-71	1975-76	1978-79	1979-80	1980-81*
1. Crude Oil Production ('000 tonnes)							
(a) ONSHORE							
AOC	176	151	104	66	53	40	48
OIL	272	1895	3084	3103	2671	2215	1241
ONGC	---	1427	3634	5279	5599	5091	4229
Total (a)	448	3473	6822	8448	8323	7346	5518
Of which							
Gujarat	---	1427	3455	4148	4238	3768	3808
Assam	448	2049	3367	4300	4085	3578	1710
(b) OFFSHORE							
ONGC	---	---	---	---	3310	4422	4985
GRAND TOTAL (a+b)	448	3473	6822	8448	11633	11768	10503

TABLE 1.3b (Contd.)

Company	1960-61	1965-66	1970-71	1975-76	1978-79	1979-80	1980-81*
2. Natural Gas Production (Million Cubic Metres)							
(a) ONSHORE							
AOC	...	...	65.24	40.33	44.33	34.73	38.14
OIL	...	...	905.25	1404.88	1256.79	1074.16	709.19
ONGC	...	...	474.41	822.06	1124.45	1115.83	933.16
Total (a) Of which	...	...	1444.90	2367.27	2425.57	2224.72	1680.49
Gujarat	...	...	464.94	773.08	907.60	840.24	838.91
Assam	...	...	979.96	1594.49	1517.86	1384.48	841.58
(b) OFFSHORE							
ONGC	...	...	...	—	385.87	541.63	673.23
GRAND TOTAL (a+b)	...	...	1444.90	2367.27	2811.44	2766.35	2353.72
* Provisional	...	Not Available					

TABLE-1.3(c)
V. REFINERY CRUDE THROUGHPUT ('000 Tonnes)

Refinery	1960-61	1965-66	1970-71	1975-76	1977-78	1978-79	1979-80	1980-81*
(a) PUBLIC SECTOR								
BPCL, Bombay	—	1966	10820	17045	24364	25450	27066	25334
CORIL/HPCL/ (VMU)/(4)	—	—	—	—	4512	4693	4821	4901
CRL, Cochin	—	—	—	—	1304	1329	1100	1319
HPCL, Bombay	—	—	2498	2294	2933	2862	2866	2912
IOC, Barauni	—	753	2191	2830	2897	2800	3130	3113
IOC, Gauhati	—	804	686	827	817	825	2285	505
IOC, Gujarat	—	409	3463	4107	4129	5251	6714	639
IOC, Haldia	—	—	—	1348	2096	2213	2492	6974
MRL, Madras	—	—	1982	2690	2616	2759	2822	2308
BRPL, Assam @	—	—	—	—	—	57	190	2611
(b) PRIVATE SECTOR								
AOC, Dighoi	6130	8267	7559	5238	534	524	408	52
BSR, Bombay (1)	446	488	476	527	534	524	408	503
CORIL, Vizag (2)	2879	3989	3541	3630	—	—	—	—
ESRC, Bombay (3)	901	1118	1175	1081	—	—	—	—
ESRC, Bombay (3)	1904	2672	2367	—	—	—	—	—
Total Crude								
THROUGHPUT (a+b)	6130	10233	18379	22283	24898	25974	27474	25837

- (1) BSR was taken over by the Govt. in Jan. 1976 and renamed as Bharat Petroleum Corporation Ltd.
 (2) CORIL was taken over by the Govt. in Dec. 1976.
 (3) ESRC was taken over by the Govt. in March 1974 and renamed as Hindustan Petroleum Corporation Ltd. in July 1974.
 (4) CORIL was merged with HPCL on 9th May 1978.
 (@) BRPL came in production on 6-2-1979.

* Provisional

TABLE-1.3(d)
REFINERY PRODUCTION

Products	1960-61	1965-66	1970-71	1975-76	1977-78	1978-79	1979-80	1980-81
TOTAL PRODUCTION	5777	9561	17110	20829	23219	24193	25794	24124
1. Light Distillates of which	1050	1770	3021	3630	4051	4295	4459	4098
LPG	8	45	169	331	383	403	406	367
Mogas	1037	1421	1526	1275	1423	1515	1512	1519
Naphtha		181	1205	1910	2120	2262	2415	2111
2. Middle Distillates of which	2593	4543	8562	10769	12079	12476	13080	12119
Kerosene	929	1463	2896	2439	2450	2514	2539	2396
ATF		128	710	925	1077	1177	1104	1000
HSD	1063	1816	3840	6285	7129	7350	7975	7371
LDO	525	789	986	946	1224	1227	1230	1110
3 Heavy Ends of which FO	2134	3448	5527	6430	7089	7422	8255	7907
Fuel Oil (Total)	1342	2455	2987	3595	3454	3425	4086	4040
Lube Oils	1641	2709	4090	5083	5332	5644	6351	6124
Bitumens	22	46	231	342	413	490	487	426
Petroleum coke	421	562	805	697	992	962	1103	1081
	13	88	151	160	155	122	99	85

* Provisional

TABLE-1.3(e)
CONSUMPTION OF PETROLEUM PRODUCTS

Products	1960-61	1965-66	1970-71	1975-76	1977-78	1978-79	1979-80	1980-81*
TOTAL (excl. RBF)	7986	11918	17912	22447	25539	28241	29883	30791
1. Light Distillates	983	1370	2697	3596	4228	4583	4460	4378
Of which :								
LPG	8	46	176	336	391	408	410	398
Mogas	859	1102	1453	1275	1391	1499	1490	1521
Naphtha	---	32	904	1836	2290	2515	2413	2324
2. Middle Distillates	4297	6225	9040	11653	13771	15172	16321	17012
Of which :								
Kerosene	2024	2455	3283	3104	3634	3952	3872	4210
ATF/Jet A-1	202	428	689	897	1041	1154	1144	1128
HSDO	1270	2405	3837	6595	7736	8638	9801	10326
LDO	671	778	1092	878	1164	1217	1266	1125
3. Heavy Ends	2706	4323	6175	7198	7540	8486	9102	9401
Of which :								
F.O.	1599	2875	3513	4279	3958	4395	4796	5337
Fuel Oils (Total)	1923	3224	4664	5781	5839	6668	7081	7415
Lubes/Greases	335	419	545	441	478	544	566	586
Bitumen	434	576	777	690	908	943	1069	1081
Petroleum coke	---	65	107	151	146	155	185	100
Others	14	39	82	135	170	176	201	219

* Provisional

TABLE—1.3(f)
REFINING CAPACITY IN THE WORLD
(as on 1st Jan., 1973)

	16 ⁶ BPCD
U.S.A.	13.46
Other Western Hemisphere Countries	8.07
Western Europe	17.42
Soviet Union	
& Eastern Europe	7.79
Africa	0.86
Middle East	2.70
Asia & Far East	7.88
World Total	58.18

(Source : United Nations : Statistical Year Book 1973)
pp. 273 (1974)

TABLE—1.3(g)
CRUDE RESERVES AND PRODUCTION IN 1975
World Crude reserves : $79,277 \times 10^6$ Tonnes
(Proved and recoverable economically)
World Crude production during 1975 : 2646.29×10^6 Tonnes
Some countries production figures

	Reserves	Production
Saudi Arabia	$15,168 \times (10^6 \text{ Ton})$	$352.394 \times (10^6 \text{ Ton})$
Kuwait	10,151	105.232
Iran	9,084	267.623
U.S.S.R.	8,140	495.00
India	141	8.283

	NATURAL GAS	
World deposits	$69,841 \times 10^9$ cubic metres	
	Reserves	Production
	($\times 10^9$ cubic metres)	(Teracalories equivalent)
U.S.S.R.	20,105	2831,000
U.S.A.	6,462	4946,534
Iran	10,613	205,240
India	88	8,508

(Source : UNITED NATIONS : Statistical Year Book 1976, p. 178-179)

TABLE 1.4(a)
INDIA REFINERIES AND CRACKING PRACTICE

	<i>Types of Refinery Units</i>	<i>Capacity MMTA</i>	<i>Cracking BPSD</i>	<i>Refining</i>
1. Assam Oil Company, Dibrui	D ₁ D ₂ /D ₀ /L/B	0.5	2300*	
2. (Bharat Petroleum) Burnah Shell, Bombay	D ₁ D ₂ /C ₀ /R/B	3.5 (50)	17000* FCC	7000* R
3. Hindustan Petroleum Corporation Ltd., (For- merly ESSO), Bombay	D ₁ /C ₀ /B	3.5	11000* FCC	
4. -do- (Formerly CALTEX), Vizag	D ₁ /C ₀ /B	1.2 (3.5)	9600* FCC	
5. Cochin Refineries Ltd., Cochin	D ₁ /Vis/R/B	2.5 (3.5)		6000* R 33,043* HDS
6. Madras Refineries Ltd., Madras	D ₁ D ₂ /C ₀ /R/Vis/B/L	2.8	5950 (C) 6460 (Vis)	2158* R 31,820 HDT

TABLE 1.4a (Contd.)

	Type of Refinery Units	Capacity MMTA	Cracking BPSD	Refining
7. Indian Oil Corporation				
Gauhati	D ₁ /C	0.75	6200	
8. "	D ₁ D ₂ /C/B/L	2.5 (3.4)	12000	
9. "	D ₁ /R/Vis	4.5 (7.3)		7500* (R)
10. "	D ₁ D ₂ /Vis/R/B/L	2.5 (5.5)	9000 (Vis)	4900* (R) 4500 HDT 13000 HDS
11. "	Mathura ¹⁻⁴	6	20000*	5000*
12. Bongaigon Refinery & Petro-chemicals (Complex)	D ₁ /R/isomerisation Unit	1		80000 150000 (isomerisation)

(Nomenclature) : D₁ : Atmospheric column, D₂ : VDC, C_g : Cat-Cracking, D_g : Dubbs cracking,

C : Thermal cracking/coking, L : Lube oil, B : Bitumen, Vis : Visbreaking, R : Reforming, HDT : Hydrotreating, HDS : Hydrodesulfurisation

1-A : Mathura Refinery Products : *CEW*, Oct. 1981, p 22, HSD : over 2MMTA, Naphtha : 8,09,000 TA, Kerosene : 6,58,000 TA, Petrol : 3,50,000 TA, LPG : 1,80,000 TA

(Fig. in brackets shows the expansions in progress)

Ref : X : *Petroleum Times* 8th March 1974, * *Oil & Gas. J. Dec 27, 1976, p. 149*

TABLE—1.4(b)

PROCESS USED BY VARIOUS LUBE UNITS

Refinery	1	2	3	4	5	6	7	8	9	10
Finished base stock capacity Tonnes/year										
1. Assam Oil Co.	x		x			x			-x	
2. Barauni Refinery	x				x		x		-x	
3. Madras Oil Refinery	x			x			x			x
4. Lube India Ltd.	x				x			x	x*	x
5. Haldia Refinery	x	x		x			x			x

Key for the Table

1. Vacuum distillation ; 2. Deasphalting ; 3. Acid alkali-treatment ; 4. Furfural extraction ;
 5. Phenol extraction ; 6. Chilling and Pressing ; 7. MEK dewaxing ; 8. Propane dewaxing ;
 9. Clay contacting ; 10. Hydro-finishing.

Note : (x) Units mentioned. x* Acid some stock.

Ref :

P.K. Goel

Himmat Singh

J. M. Segar

K. K. Bhattacharya

B. S. Gulati

: Chemical Age of India

April 1971 : p. 51

TABLE 1.4(c)

TRANSFORMER OILS

Apar Pvt. Ltd. Bombay	15,000 MT	Total licenced capacity : 65,000 MT
Nagpal Ambadi Petro-chemical Ltd. Madras	15,000 MT	Production 35,000 MT
Savita Chemicals Ltd Bombay	10,000 (licensed for 40,000 MT)	
Universal Petrochemicals Ltd. Calcutta (Registered only)	10,000 MT	(Source : N. D. Desai 2nd LAWPS Symposium January 1981, I.I.T. Bombay P-4)
Lube India Ltd (Base Stock for Transformer oils only)	17,000 MT	

TABLE 1.5

A VISTA OF INDIAN PETROLEUM INDUSTRY

1866	First oil well, Nahorpung (Assam)
1890	Discovery of Digboi oil field
1893	Refinery at Mergherita
1899	A O C. Registration
1923	First geophysical survey by A O.C
1953	Discovery of Nahorkatiya field
1954	ESSO Establishment
1955	Burmah Shell
1956 (August)	ONGC was set up
1957	Caltex
1958 (18th February)	O.I.L India
1959	LUMEJ field
1960	Ankaleswar Oil field 1960—11P. Dehra Dun
1961	Discovery of Rudrasagar
1961	Gas field Kalol
1962	Noonmathi Refinery (Rumanian Collaboration)
1962	Gas field, Sonand
1963	Nawagam field
1963	Crude Oil produced by O.I.L
1964	Lakwa Oil field
1964	Barauni Refinery (Soviet Collaboration)
1964 (Sept)	Establishment of I.O C
1965	Koyali Refinery (Soviet collaboration)
1966	Cochin Refinery (Phillips Petroleum)
1968	Gelki Oil field
1969	Madras Refinery (National Iranian and AMOCO)
1970 (Feb)	Lube India Refinery foundation
1972 (Jan.)	Bongaigon Refinery & Petrochemical Complex foundation
1973	Haldia Refinery (French & Soviet)
1973	Acquisition of jack up rig Sagar Samrat
1973	ONGC entered into agreement with Iraq for exploration in southern parts of Iraq.
1974	Bombay High Discovery, Haldia Trial runs.
1974	Oil found in Bombay High,
1974	Taking over ESSO by G.O.I.
1976	Discovery of Bassein, near Bombay High
1976 (May)	Commercial production of oil from Bombay High two wells.
1976	Baramura gas field, Tripura
1978	Mathura Refinery foundation
1978	Mahim gas field at Bombay
1980 (Sept.)	Oil struck in Godavari delta (Offshore one well & on shore two wells near Narsapur)
1981 (Sept.)	Take over of Burmah Oil & A.O.C. by Government of India
1982	Kharsang, Oil field (Oil Ltd.) Arunachal
1982 (August)	First LNG plant, Duliajan

TABLE 1.6
CHARACTERISTICS OF CRUDES PROCESSED IN INDIA

Crude Characteristics	Nahorkatia (Assam)	Ankleswar (Gujrat)	Light Iranian	Darius	Digboi
• API	31.0	0.8710	34.4	34.1	
Sp-gravity 60/60°F	0.8710	47.0	0.8535	0.8280	0.84
Sulphur, wt %	0.16	0.05	1.35	2.47	0.20
Pour point, °C	30	15	-21	-40	29.8
Total C ₄ minus wt. %	2.5	4.36	1.80	1.65	
C ₃ to 140°C wt. %	17.0	23.14	14.45	15.85	
RON clear	75.0	59.0	55.0	58	
140-250°C, wt. %	20.5	27.5	19.30	15.5	
Freezing point, °C	-60	-42	-56	-51	
Sulphur, wt. %	0.06	0.002	0.18	0.30	
Smoke point, mm	14	30	22	25	
250-371°C, wt. %	24.0	23.2	21.80	20.5	
Sulphur, wt. %	0.22	0.025	1.10	1.72	
Diesel index	39	66	53	55	
Pour point, °C	6	6	0	-3	
371°C-i-wt. %	36.0	21.8	42.65	46.5	
Sulphur, wt. %	0.38	0.12	0.53	4.2	
Viscosity cS @ 50°C	160	25	700	560	
Pour point °C	51	48	48	25	
Salt content NaCl wt. %	.0005				0.0005

TABLE 1.6 (Contd.)

	Bombay High	Gelki	Digboi
API	36.2	32.1	
Sp. gravity	0.8440		
Sulfur wt %	0.12		
Pour point °C	27	33	5 (CS)
Viscosity at 37.8°C	—	—	IBP : 72°C
	Distillation Data, Volume % (Cumulative)		(75°C)
°C	4.5	3.0	0.5
50	11	9.7	4.0
100	23	17.5	19.0
150	29	21.7	25.0
175	33.5	25.6	30.0
200	36	29.5	35.0
225	43	33.1	41.0
250	54	38.9	45.0
275	60	44.6	54.5
300	65	49.2	
325	70	54.7	
350	74	57.0	
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CHAPTER 2

Petroleum Processing Data

2.1 Evaluation of Petroleum

Petroleum is classified into mainly three congenial types as :

1. Paraffinic base
2. Mixed base or Intermediate and
3. Naphthenic base.

Some authors have referred to the naphthenic base as asphaltic base. The name naphthenic is more convincing as it represents the homologous series whereas asphalt is a polymeric condensed material having very high carbon to hydrogen ratio of no equable nature of general formula. Although the categorisation into these three types may not be very accurate and brief, it serves, without any reservations the purpose. Knowledge of base of a crude is very essential as it depicts, even though not fully the usual properties enmass and can adequately inform the refiners about the difficulties in processing too.

Irrespective of the base of the crude all the hydrocarbon series listed in Chapter 1 are present in all crudes, but to different extents.

Mallison classified the crude exclusively on the basis of residuum, a material left behind after distillation of fractions.

Accordingly :

Residue containing more than 5% paraffins is paraffinic crude

Residue containing less than 2% paraffins is naphthenic base

Residue containing 2%—5% paraffins is considered as mixed base

The proper method of evaluation of crude started with U.S.

Bureau of Mines, which designated eight different bases of crude. The basis of classification begins with two chosen fractions, Key fraction No. 1 and Key fraction No. 2 as given below :

Key fraction No. 1 (kerosene) has a boiling range of 250°C-275°C at normal pressure

Key fraction No. 2 (Lube) has a boiling range of 275°C-300°C at a pressure of 40 mm Hg ; i.e. 389°C-422°C at 760 mm pressure

The API gravities of these fractions are found out and the base of crude then characterised as

When Key fraction No. 1 has : 40 or more API gravity it is paraffinic less than 33 API gravity, it is naphthenic and in the range of 33-40 API gravity, it is mixed base.¹

When Key fraction No. 2 has : 30 or more API gravity then it is paraffinic ; less than 20 API gravity it is naphthenic and between 20-30 API gravity it is mixed base.

Above distinct classification dispels any ambiguity or dissension, however in the case of mixed base crudes, the nearness to extremities is mentioned for avoiding any moots. Say a key fraction No. 1 of a crude is having 39 API, this without any doubt, is mixed base but more oriented towards paraffinicity rather than naphthenicity. Similarly an API 33.3 is not only mixed base but tilted towards naphthenic nature rather than paraffinic nature. In such cases it is judicious to use (for the above fractions as) mixed base (paraffin), mixed base (naphthene) respectively.

In case of key fraction No. 2, often wax on wax free term is proposed. If the pour point is less than 3°C, for this fraction then the base is followed by the 'Wax free' term ; otherwise it is followed with subscript 'waxy'.

Earlier days, classification based on the location of crude was habitual such as Pennsylvania crudes classified as paraffinic base and Gulf coast crudes as naphthenics. These ideas need not be any more entertained, as location or formation can never give the idea of crude. Some crudes rich in aromatic series were also classified as aromatic crudes or benzenoid base crudes. As all naphthenic crudes give plentiful aromatics such formal classifications need not be attended.

API (American Petroleum Institute) gravity : This is defined as :

$$\text{Deg. API} = \frac{141.5}{\rho} - 131.5 \quad (2.1)$$

where, ρ = sp. gravity of fraction at 15.6°C/15.6°C

API gravity magnifies the sp. gravity of fractions. As the sp. gravity of close boiling cuts usually lies very close to each other, this type of magnification is essential. For a blend, the API gravity is given as :

$$(\text{API})_{\text{mix}} = (\text{API})_a \times W_a + (\text{API})_b \times W_b + (\text{API})_c \times W_c + \dots \quad (2.2)$$

Thus API gravity of a mixture is equal to the sum of the individual API gravity of a component multiplied by corresponding weight fraction in the mixture.

2.1.1. U.O.P. CHARACTERISATION FACTOR (K)^{2a}

Characterisation factor is of immense utility in refinery calculations. Besides it has got capacity to predict the qualities of crude, it can also provide with many valuable data on fractions. API gravity and molecular weight as other parameters, it can give almost all necessary information about the fraction, right from physical properties to tendency of cracking.

The relation is given by

$$K = \frac{\sqrt[3]{R}}{0.823} \quad (2.3(a))$$

(Original K factor was formulated on $^{\circ}R$ and ρ at 60°F.)
where R = average boiling point $^{\circ}K$.

ρ = sp. gravity at 15.6°/15.6°C

For paraffinic base of crude oil K is 12.5 and above, and if it is less than or equal to 10, the base of the crude is denoted as naphthenic. For a fraction, usually average boiling point will coincide with 50% boiling point when Engler slope is less than 3. Waston and Nelson replaced the term average boiling point by molal average boiling point, but retaining the index values for characterisation purpose^{2b}. Molal average boiling point is better suited for a wide boiling fraction with a slope more than '3' in Engler distillation.

If the characterisation factor is 12.5, the crude is classified as paraffin base and less than 10, is said to be naphthenic base.

Intermediate values are regarded as mixed base crudes. K -value of a mixture is the sum of the components ' K ' value multiplied by their weight fractions in mixture.

$$K_{mix} = K_1W_1 + K_2W_2 + K_3W_3 \quad (2.3(b))$$

where, W_1, W_2, W_3 are weight fractions of different components.

K_1, K_2, K_3 are respective characterisation factors.

2.1.2 CORRELATION INDEX

Like characterisation factor correlation index is also related to boiling point and gravity, however its use is marginal :

$$\text{Correlation Index (C. I.)} = \frac{486404}{T_B} + 473.7 \rho - 456.8 \quad 2.4$$

where T_B = boiling point (molal) °K

ρ = sp. gravity at 15.6°C/15.6°C

Correlation index for paraffins is taken as zero and for aromatics, it is taken as 100. The value is not quantitative hence a relative indication of the groups is only possible.

2.1.3 DISTILLATION CHARACTERISTICS

Crude Assay analysis

Distillation characteristics of a crude are assessed by performing a preliminary distillation called 'True Boiling Point' analysis (TBP). This pulse test enlightens the refiners with all possible information regarding the percentage quantum of fractions, base of crude and the possible difficulties beset during treatment operations etc. Information supplied by this distillation forms the basis of design of distillation columns and thus represents the veridity of crude distillation.

TBP Apparatus

Pursuits for development of such kind of stills were left with Peters, Podbielniak stills. A less costly laboratory still with proper adjustments and controls may also be tried, when situation demands. A thorough rectification system constituting 10 to 12 stages forms the operation. Modern stills are instituted to distill at least 2 liters of stock per charge. Larger capacities are preferable as good amounts of higher boiling stocks can be obtained for testing. Heat losses in industrial operations are managed by lagging, but in such small stills hot air circulation

through the jacket, surrounding the rectifier section, ensures the minimum thermal losses. Top of rectifier is usually fitted with an efficient air cooled reflux condenser, which also indicates the temperature of the fraction leaving for the condenser system.

The condensate collects into a graduated cylinder, which is in fact connected to a vacuum producing device. The vacuum device must have sufficient displacement capacity to ensure satisfactory operation. For this reason, a displacement of 0.2 to 0.5 cubic meters of air or vapor is required for stills of capacity 2 to 5 liters. It is also essential that distillation proceeds at a constant rate. Too high a rate results in flooding and lower rates produce imperfect fractionation. Observations have revealed that rate of distillation in the beginning is very high, but the rate of distillation decreases with increasing boiling point of the stock. Hence a careful heating and condensation system is required. A good rate of distillation prescribed for atmospheric

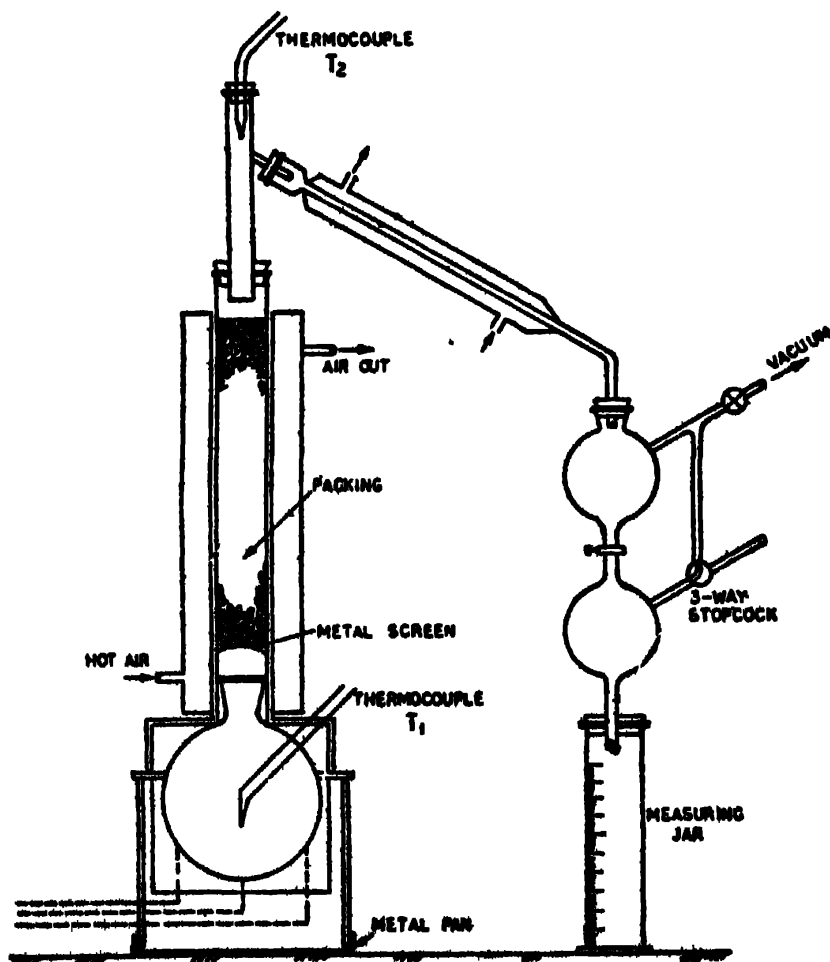


FIG. 2.1 TBP Apparatus

operation is 1% distillation in 2 minutes and under vacuum it drops to 1% in 3 to 5 minutes. Further, the system in no way should suffer while removing the condensate during vacuum distillation.

The necessity of vacuum distillation is mainly to prevent the thermal degradation of high boiling stocks. The high boiling—stocks are prone to crack when exposed to a temperature of 370°C or more. Vacuum distillation reduces the boiling point of the fraction, and for every pressure there is a definite boiling point. These boiling points obtained under the exposed pressures or vacuum should be corrected back to the normal pressure (760 mm) operation.

A sketch of the TBP apparatus is furnished in Fig. 2.1

Boiling point corresponding to a particular pressure can be converted to normal boiling point with the help of Fig. 2.2(a).

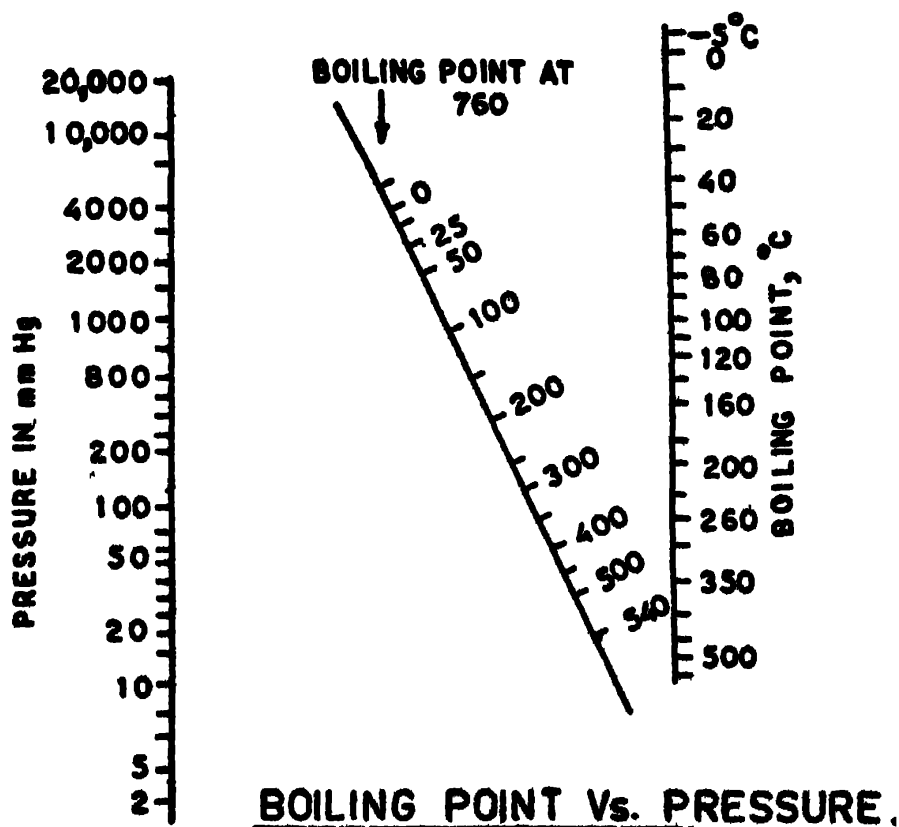


FIG. 2.2(a) Boiling Point Vs. Pressure

Taken from Petroleum Refinery Engineering
W. L. Nelson (c)

Used with the permission of the McGraw Hill Book Comp.

Figs 2.2(b) and (c) are useful when very high pressures or low pressures are involved.

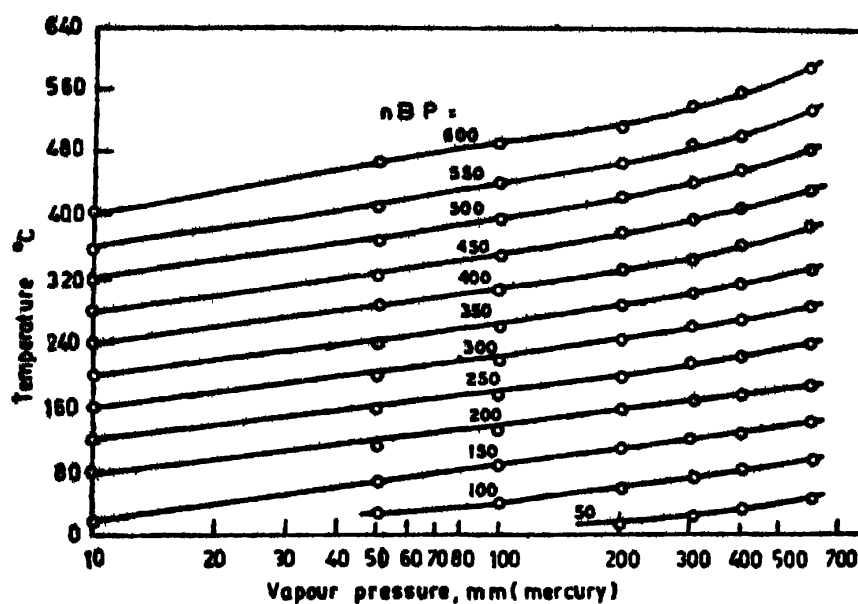


FIG. 2.2(b) Normal Boiling Point Variation at Low Pressure

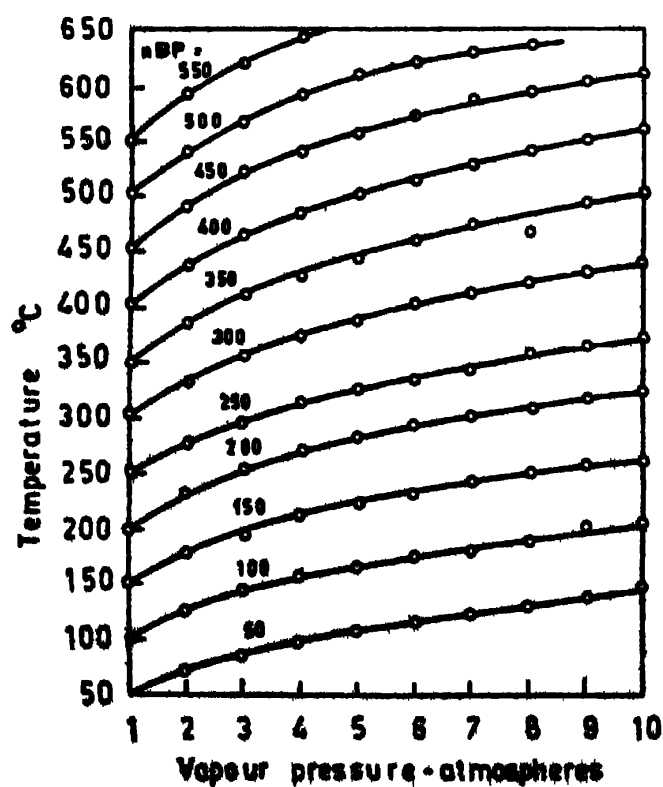


FIG. 2.2(c) Normal Boiling Point Variation at High Pressures

The data collected are usually presented in the graphical form as shown in Fig. 2.3 and goes by the name TBP curve.

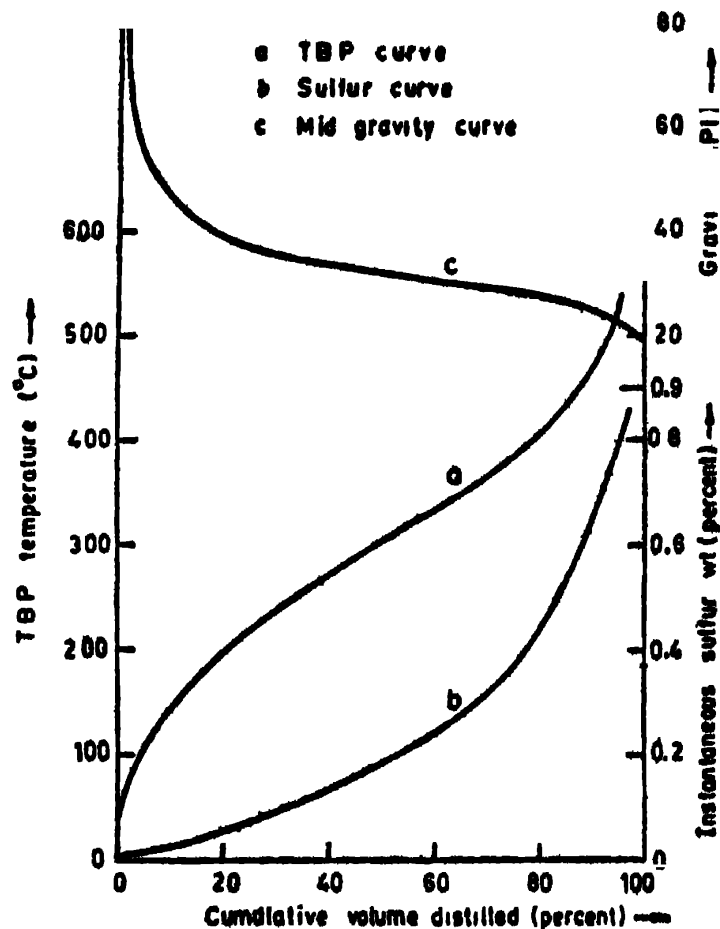


FIG. 2.3 TBP Crude Assay Curve
 Curve a = Temperature *Vs.* Volume
 b = Sulfur *Vs.* Volume
 c = Gravity *Vs.* mid percent

2.1.3.1 Equilibrium Flash Vaporisation (EFV) :

While in continuous fractionation system such as TBP, always a thorough contact between vapor and liquid exists ; in equilibrium flash vaporisation, vapor is kept cohesively with liquid at some temperature and a sudden release of pressure quickly flashes or separates the vapor from the mixture without any rectification. By successive flash evaporations like this the stock can be progressively distilled at different increasing temperatures. Experimentally this type of distillation may not be suggested as interconversion from one type of distillation (say TBP to EFV) to other is always available.

2.1.3.2 Engler distillation : (ASTM-D-86)

It is also known as ASTM distillation and is supposed to be like EFV, a nonfractionating distillation system, distinguishing itself as differential distillation. All fractions are specified by this distillation only. It is a simple distillation carried out with standard ASTM flasks of 100, 200, 500 ml capacity. The data obtained is similar to TBP data and interconvertability is resorted wherever essential.

2.1.3.3 Humpel Distillation

Information about this in modern literature is not abundant, it is considered as a semi-fractionating type of distillation like Saybolt's, Where TBP data is insufficient, this can be used, as it nears the TBP characteristics of distillation.

Different^s types of boiling points and functional values

<i>Average boiling point</i>	<i>Physical property for which it is distinct</i>
1. Volume average	Use for liquid viscosity, specific gravity
2. Weight average	Critical temperature
3. Molal average	Characterisation factor, thermal expansion of liquids
4. Mean average	Molecular weight, sp. gravity Heat of combustion, sp. heat, etc.
5. Cubic average	For additive properties ; viscosities are additive when expressed on cubic average

2.1.4 * AVERAGE BOILING POINTS

Because of a fraction boiling regularly or haphazardly over a wide range, it is essential to represent the boiling point of the fraction by some method, which can specifically denote certain physical properties. For narrow boiling cuts (TBP slope less than 2) all the above mentioned boiling points tend to be equal.

Volume average boiling point is based upon the boiling temperature of different cuts of the fraction. Usually cuts are chosen at regular intervals.

Thus for whole crude, it may be represented as :

(Volume average BP)

$$T_B = \frac{t_{10\%} + t_{20\%} + t_{30\%} + t_{40\%} + t_{50\%} + t_{60\%} + t_{70\%} + t_{80\%} + t_{90\%}}{9} \quad (2.5a)$$

If such data is not available then it may be defined as

$$(\text{Volume average BP}) T_B = \frac{t_{30\%} + t_{50\%} + t_{70\%}}{3} \quad (2.5b)$$

where all percentages are in volumes.

If the fraction is boiling over a narrow range of temperature then $t_{50\%}$ may be accepted as average boiling point.

($t_{10\%}$ means the temperature indicated when exactly 10% of the stock is collected during distillation.)

Weight average: In this case instead of volume, weight fraction is chosen for evaluating boiling point. Thus

$$(\text{Weight average BP}) T_B = \frac{t_{10\%} + t_{20\%} + \dots + t_{90\%}}{9} \quad (2.6)$$

where percentage calculations are based on weight.

Molal average: This is based upon boiling temperatures at different mole fractions. It is no doubt a perilous job as determination of molecular weight for each cut is not practiced.

$$(\text{Molal average}) T_B = \frac{tx_1 + tx_2 + tx_3}{x_1 + x_2 + x_3} \quad (2.7)$$

where x_1, x_2, x_3 are mole fractions.

t_1, t_2, t_3 are corresponding boiling points.

Mean average: This is the temperature at which some physical properties like specific heat, specific gravity etc. of a fraction are found out by taking the mean of temperature levels:

sp.heat at temp. $t' = c'_p$ and $t'' = c''_p$

$$\text{average sp. heat at } \frac{(t' + t'')}{2} = \frac{(c'_p + c''_p)}{2}$$

Mean average and average boiling point coincide for a blend of two components and these are related to TBP slopes as shown in Fig. 2.6 a and b.

Cubic average: Some properties like viscosity seem to be additive when cubic average is taken into consideration, rather than mean average, or molal average thus,

$$(\text{cubic average}) T_B = [V_a(t_a)^{1/3} + V_b(t_b)^{1/3} + V_c(t_c)^{1/3}]^3 \quad (2.8)$$

All these boiling points are interconvertable.

Interconvertability of boiling points can be worked out by knowing the slope of distillation curve of a fraction. The method of finding out the slope for ASTM/TBP/EFV is the same.

TBP slope is given as $\frac{t_{70\%} - t_{10\%}}{60}$ i.e. °t/percent ; where

70% and 10% are volumetric boiling points on vaporization curve. The conversion of TBP slope to ASTM or EFV slope can be done with the help of Figs. 2.4 or 2.5 (a) and (b). Fifty percent

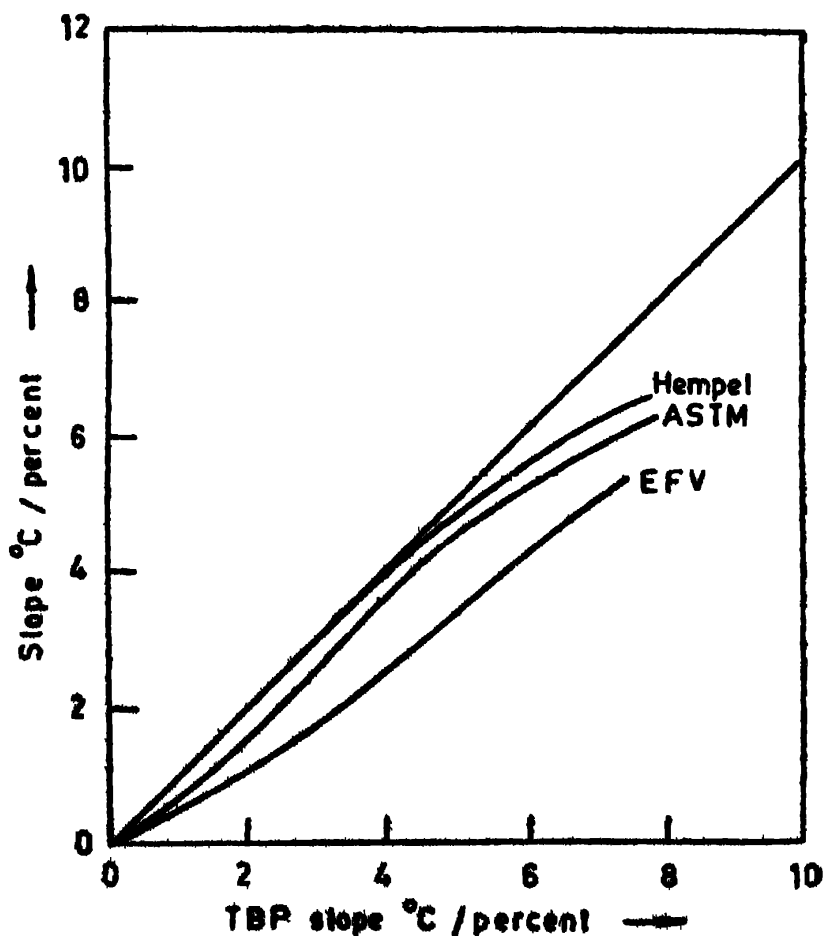


FIG. 2.4 Different Slopes and Interconversion.
(By courtesy Oil and Gas Journal)

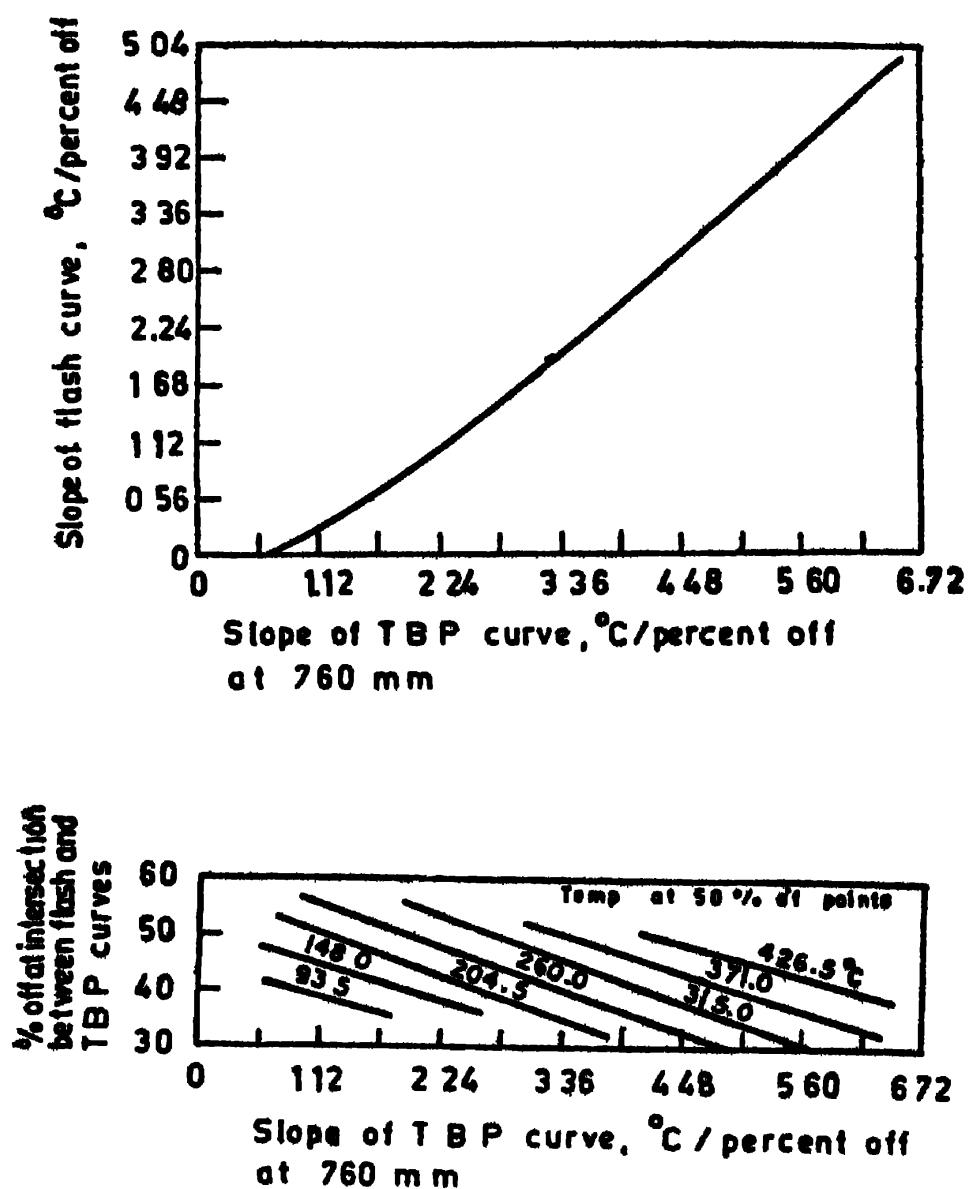


FIG 25(a) ASTM—Flash Slope Interconversion and their Intersection points
 From American Petroleum Refining
 By H S Bell (3rd Edition)
 With permission from Brooks/Cole Publishing Co.
 Owners of Van Nostrand Company

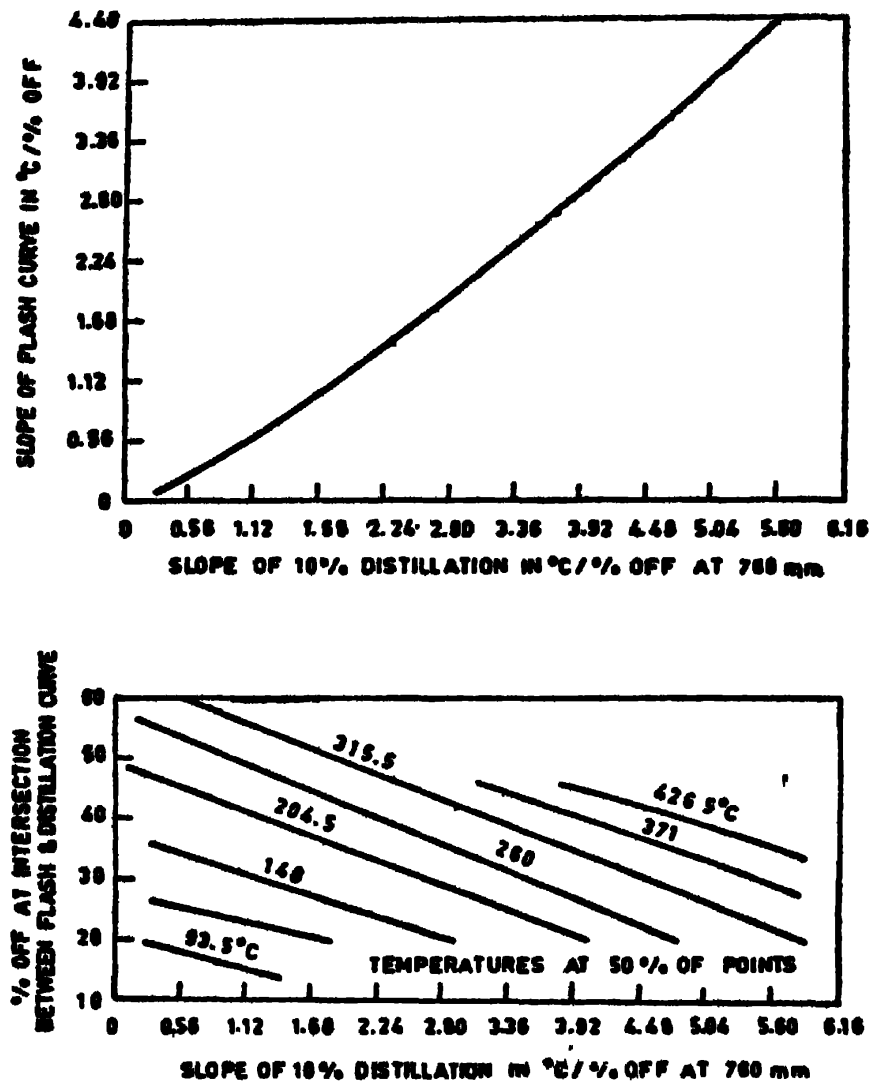


FIG 2.5(b) TBP—Flash Slope.
 Interconversions and their Intersection Points
 (From American Petroleum Refining By H S. Bell
 3rd Edition. With Permission from Brooks/Cole
 Publishing Co.
 Owners of Van Nostrand Company)

boiling points of ASTM curves can be calculated by knowing the slope of TBP curve of a crude and its 50% boiling point⁴. The correction factor is incorporated in Table 2.1. Similarly from ASTM or TBP slopes, EFV 50% boiling point can be found out from Fig. 2.6(a).

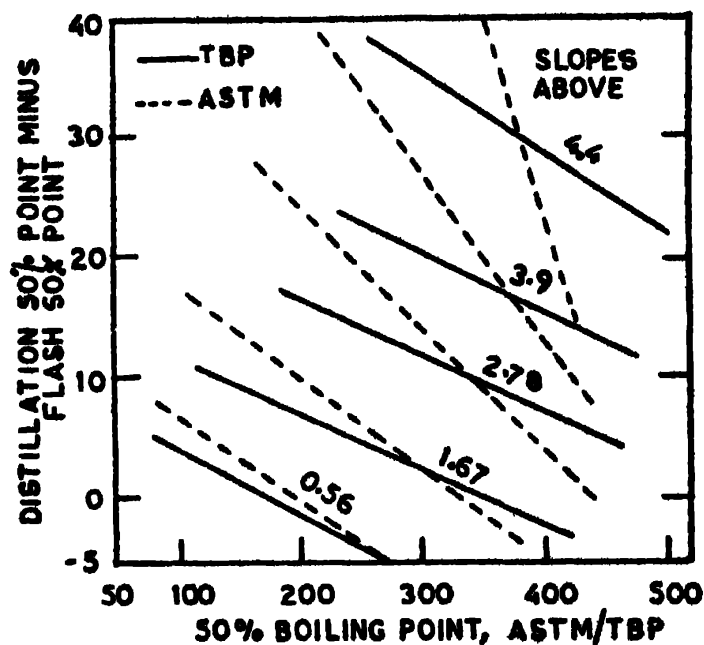


FIG. 2.6(a) Relation Between 50% Boiling Points
(Taken from Petroleum Refinery Distillation R. N. Watkins
2nd Edition Copy Right 1979, by Gulf Publishing Co.
Houston, Texas)

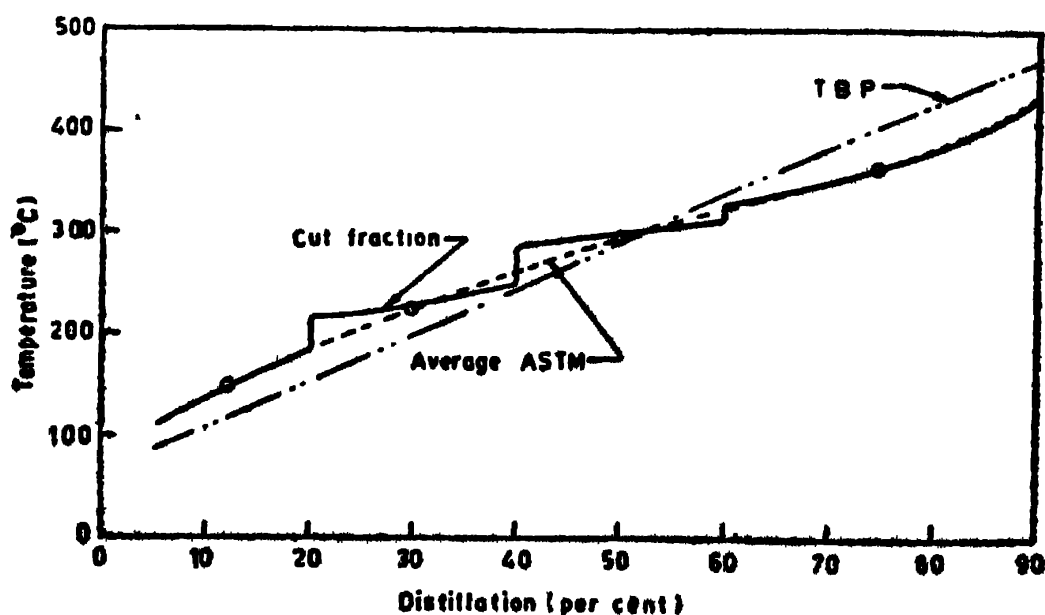


FIG. 2.6(b) ASTM cut fraction curves

TABLE 2.1
RELATION BETWEEN 50% BOILING POINT OF ASTM AND TBP

TBP 50% BP	Correction to be added to TBP 50% BP				
	TBP Slopes				
	1	3	5	7	9
°C					
37.8	-2.8	-9.5	—	—	
93.3	-1.2	-3.3	-6.7	—	
119	-0.56	-1.7	-3.3	-13.4	-25.0
204	+0.56	+1.2	-1.2	-9.0	-17.0
260	+1.2	+2.2	+1.3	-4.06	-10.0
315.5	+2.2	+5.0	+3.3	-0.56	-5.6
371		7.8	+8.3	+5.6	+0.56
428			+11.7	11.0	9.0

Slopes of different boiling point curves are also easily interconvertible and Figs. 2.4 and 2.5 (a, b) help in such conversions.

2.1.4.1 Boiling point—pressure

Under equilibrium, for every liquid there is a definite vapor pressure for a definite temperature and the vapour pressure increases with increase of temperature and vice-versa ; though not linearly. Interestingly when vapour pressure and temperature are plotted on a semi-log paper, a straight line relation is revealed, this relationship although may change from groups to groups like alcohols, ketones, paraffins, aromatics etc. it follows in case of hydrocarbon groups without any exception.

Claussius-Clapeyron equation can also be used where there is data available, on latent heat of vaporization

$$\ln \frac{P}{P_0} = \frac{\lambda}{R} (1/T_0 - 1/T) \quad \dots \quad (2.9)$$

where, P_0 , P are vapour pressure at T_0 , T absolute temperatures

λ = molal latent heat of vaporization at T

R = gas constant in corresponding units

Relations of Cox, Perry,⁵ Meyer,⁶ are worth mentioning in this connection. The boiling points at high and low pressures are also available in literature.⁷ Conversion of boiling point at one pressure to another can be done with the help of Fig. 2.2(b) & (c), as shown already.

Problem 2.1

Use the following data of a crude ; Trinidad blend, to plot crude assay curves. Assess the quality of crude and various fractions.

<i>Trinidad blend</i>		
Whole crude	Gravity °API	33.6 (0.8570)
	Sulfur, wt. %	0.23
	Pour point, °C	+14
	Viscosity (SUS) at 20 °C	47
	at 56 °C	38
	C ₄ and lighter, vol. %	0.58
Light straight run	Range, TBP °C	C ₆ —93
	Yield, vol. %	3.28
	Gravity, °API	69.6 (0.7035)
	Sulfur, wt. %	0.01
	Motor octane, clear	73 2
Cat.reformer feed	Range, TBP, °C	93—175.0
	Yield, vol. %	11.71
	Gravity, °API	46.9 (0.7932)
	Sulfur, wt. %	0.20
	Arom+naph, vol. %	69.7
Heater-oil dist.	Range, TBP, °C	175.0—286
	Yield, vol. %	30.51
	Gravity, °API	34.8 (0.8508)
	Sulfur, wt. %	0.10
	Blend pour pt. °C	1
	Cetane index	40.2
Furnace-oil dist.	Range, TBP, °C	286—325
	Yield vol. %	13.69
	Gravity °API	31.3 (0.8692)
	Sulfur, wt. %	0.20
	Blend pour pt. °C	5
	Cetane index	48.5

Light FCU feed	Range, TBP, °C	325–365
	Yield, vol. %	9.05
	Gravity, °API	29.0 (0.8816)
	Sulfur, wt. %	0.32
	CA, wt. %	12.5
	Nitrogen, wt. %	0.024
Heavy FCU feed	Range, TBP, °C	365–542
	Yield, vol. %	26.97
	Gravity, °API	28.1 (0.8865)
	Sulfur, wt. %	0.37
	CA* wt. %	12.2
	Nitrogen, wt. %	0.038
	Equiv. nickel, ppm	0.1
Reduced crude	Range, TBP, °C	542+
	Yield, vol. %	4.22
	Gravity, °API	20.0 (0.9340)
	Sulfur, wt. %	0.89
	Rams. car, wt. %	4.8
	V+Ni, ppm	10

* CA% = Aromatics

Sol :—Fig. 2.1 shows the TBP characteristic curves of the crude. Close observation reveals the following :

1. Sulfur and sp. gravity increases regularly from low boiling fractions to high boiling fractions. It can be treated as a low sulfur-crude (0.23% sulfur on whole crude basis) ; however desulfurisation is recommended for fractions (especially catalytic reforming feed stocks). Gravity shows that it is of mixed base origin, although confirmation is essential.
2. Fifty percent of the crude can be distilled below 300°C, it shows that the crude is dominant in lighter fractions. It is a source of gasoline of quality and quantity and may be utilised even without desulfurisation. Good solvent of end point 180°C can also be obtained.

3. Diesel fuels or heating oils (upto 350°C) form the main products (up to 40%). Diesels are of good quality (cetane no. 40) and pour point is also convenient for regular usage.
4. Vacuum distillation is expected to separate the catalytic cracking feed stock usually known as gas oil. The residue from the vacuum distillation column may be utilised as bitumen rather than for coking operations, as it contains less carbon residue it may not give good quantity of coke.

Problem 2.2

Use the TBP data of the above problem and find out TBP, ASTM, EFV slopes.

Solution :

TBP slope is found out by knowing the temperatures of distillation at 70% and 10% (Fig. 2.1) off.

$$\text{TBP slope} = \frac{355-138}{60} = 3.61^{\circ}\text{C/per cent}$$

With the help of Fig. 2.4 slope of TBP is converted to ASTM i.e. 3.06°C/per cent. Similarly Fig. 2.4 gives slope of TBP to slope of EFV i.e. 2.1°C/per cent or Fig. 2.5 a & b are also helpful.

Problem 2.3

Find the percentage intersection of TBP and ASTM & TBP and EFV from the data of problem 2.1.

Solution :

Firstly the 50% BP on TBP curve is found out as equal to 302°C. TBP slope is given (from above problem).

From Fig. 2.5(a) the 50% B.P. and slope of the curve will give the percent off intersection points between flash curve and TBP i.e. 39% similarly for ASTM it is obtained from Fig. 2.5(b).

From the points of intersections, with the corresponding slopes, straight lines can be drawn as shown in Fig. 2.6(b).

Problem 2.4

From the data of problem No. 2.1, compute the vaporisation curves of ASTM and EFV for the whole range. Repeat it, by choosing cuts of 5 to 20%, 20 to 40%, 40 to 60% and 60 to 90% to explain the nature of cut fraction curve of ASTM.

Solution :

Use the slopes obtained in problem 2.2. Locate the 50% boiling point with the help of Table. 2.1.

Slope of TBP $3.61^{\circ}\text{C}/\text{per cent}$

50% TBP point 302°C .

Corresponding ASTM correction is $+4^{\circ}\text{C}$ approximately. Add this to 50% TBP point i.e. 306°C , which is ASTM, 50% boiling point. At this point draw a straight line with a slope of $3.06^{\circ}\text{C}/\text{percent}$ to get ASTM curve. Similar procedure is adopted for EFV also. EFV slope is $2.1^{\circ}\text{C}/\text{per cent}$ and 50% EFV point is obtained from Fig. 2.6(a). For a cut fraction 5 to 20% ; the slope and 50% boiling point of this fraction is computed assuming that this fraction represents 100% fraction.

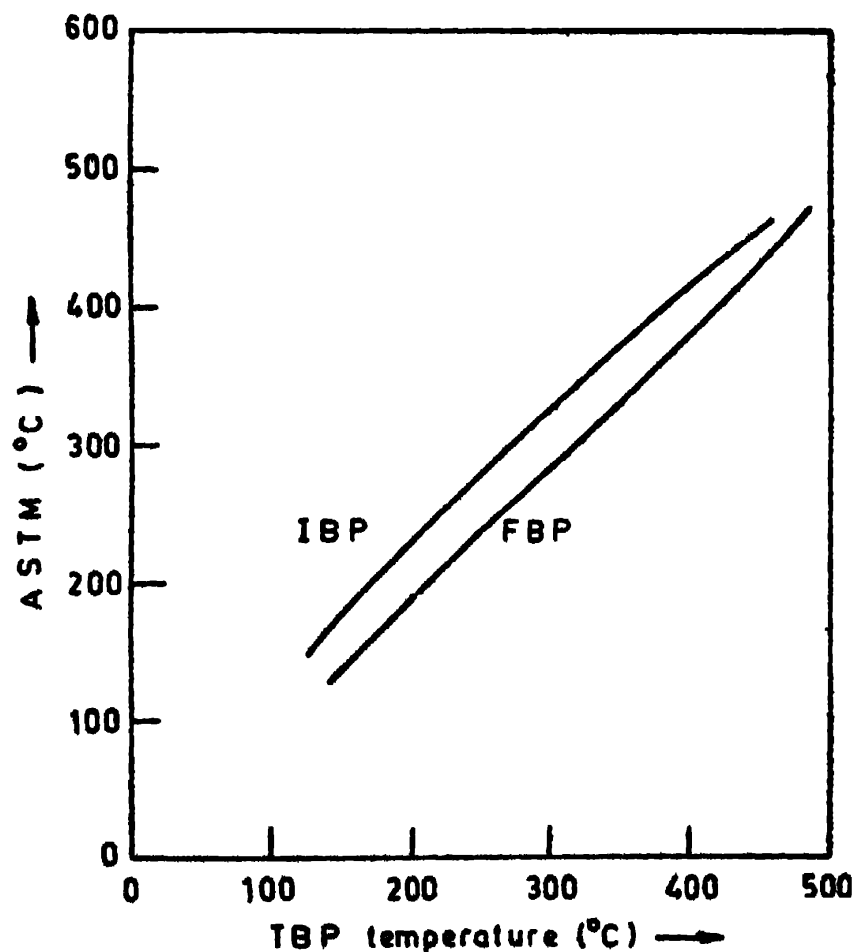


FIG. 2.7(a) Relation between IBP & FBP of ASTM and TBP.

From Petroleum Refinery Distillation, 2nd Edition by R. N. Watkins (c) 1979 used with permission from Gulf Publishing Company, Houston, Texas.

So the slope is found out by locating 70% and 10% distillation points of this fraction which correspond to

$$\frac{20 \times 70}{100} = 14\% \text{ of the fraction}$$

$$\frac{20 \times 10}{100} = 2\% \text{ of the fraction}$$

(add initial 5% to make 7%)

$$\text{Hence the slope is } \frac{t_{14\%} - t_{7\%}}{60} = \frac{160 - 110}{60} = 0.83^\circ\text{C/per cent}$$

$$\text{The approximate mid point is } \frac{5\% + 20\%}{2} = 12.5\%$$

At 0.83 TBP slope and 50% b.p. ($150^\circ.8\text{C}$)

ASTM Slope is (Fig. 2.4) = 0.48

Converting TBP 50% point to ASTM 50% point as in the above case (or use Fig. 2.7(b)) ASTM 50% b.p = 151.8°C .

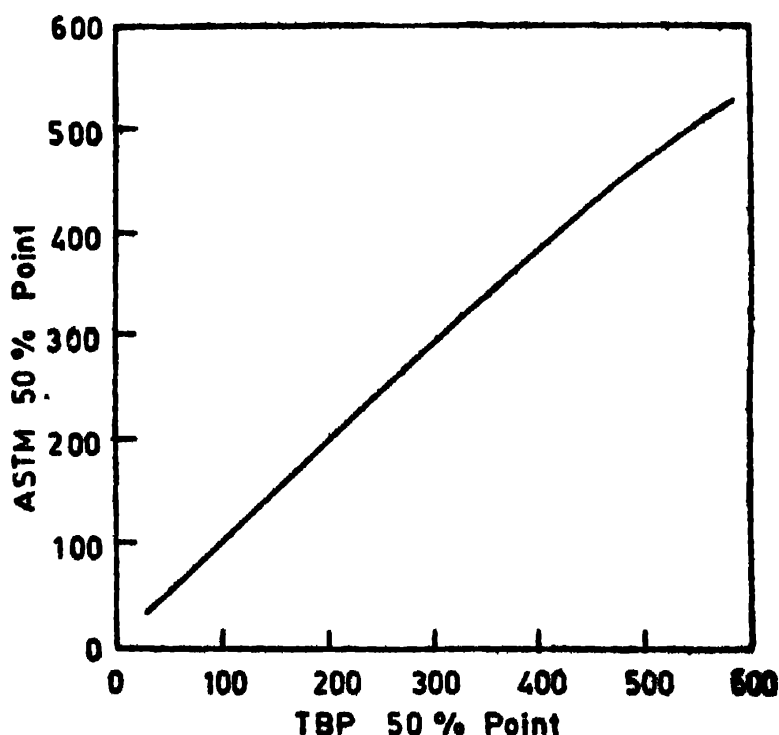


FIG. 2.7(b) Relation between TBP and ASTM 50% boiling points

(From Petroleum Refinery Distillation 2nd Edition by R. N. Watkins (c) 1979 used with permission from Gulf Publishing Company, Houston, Texas).

IBP (5% point on TBP curve) = 98.9°C.

Corresponding IBP of ASTM is found out from Fig. 2.7(a). Similarly FBP of TBP is converted to FBP of ASTM with the help of Fig. 2.7(a). When it is not possible to obtain any of these IBPs or FBPs, arithmetic technique can be used to compute.

$$\begin{aligned}\text{ASTM(IBP)} &= \text{ASTM(50\%)} \text{ b.p.} - \text{ASTM slope} \times 50\% \\ &= 151.8 - 0.48 \times 50 = 117.8^\circ\text{C}.\end{aligned}$$

Like this for all these cuts, an attempt is made to convert into ASTM fractions, as shown below :

1st cut 5–20%

$$\text{ASTM Slope} = 0.48$$

$$\text{ASTM 50\% b.p.} = 151.8^\circ\text{C}$$

$$\text{ASTM IBP} = 117.8^\circ\text{C}$$

FBP of 1st fraction (TBP) forms the IBP of 2nd cut

	2nd cut (20-40%)	3rd cut (40-60%)	4th cut (60-90%)
TBP slope	0.44	0.51	1.19
ASTM slope	0.28	0.36	0.72
TBP 50% b.p.	232°C	296°C	375°C
ASTM 50% b.p.	225°C	296°C	362°C
TBP (IBP)	195°C	268°C	330°C
TBP (FBP)	268°C	330°C	456°C
ASTM (IBP)	220°C	286°C	330°C
ASTM (FBP)	250°C	312°C	430°C

Such a cut fraction curve is shown in Fig. 2.8(b).

Problem 2.5

From the data of problem 2.1, find the characterisation factor of the crude on the whole basis; also on the basis of choosing three fractions of equal volume.

Solution :

Evaluate first. Average boiling point, on the whole crude

$$\text{basis. i.e. } \frac{t_{10\%} \dots t_{90\%}}{9}$$

$$= \frac{132 + 193 + 235 + 270 + 305 + 330 + 362 + 407 + 455}{9}$$

$$= 298.8^\circ\text{C}.$$

Average ρ : 0.8570. Obtain 'K' by substituting this value in

$$K = \frac{\sqrt[3]{(298.8+273)}}{0.8570 \times 0.823} = 11.72 \quad \dots \quad \text{I}$$

Average boiling point on the basis of $\frac{t_{80\%} + t_{60\%} + t_{40\%}}{3} = 374^\circ\text{C}$

slope TBP = $3.81^\circ\text{C}/\text{percent}$

correction to be applied to convert average boiling point to Molal average boiling point (from Fig. 2.8(a) and (b)) = -62°C i.e. 312°C .

Average density of the fraction

$36^\circ\text{API} = 0.8448 \quad \text{gm/cc}$

$32^\circ\text{API} = 0.8654 \quad \text{-do-}$

$29^\circ\text{API} = 0.8816 \quad \text{-do-}$

Average = 0.8673 gm/cc.

$$K = \frac{\sqrt[3]{312+273}}{0.823 \times 0.8673} = 11.72 \quad \dots \quad \text{II}$$

I and II show the 'K' factor same

Now choose 3 cuts as

Cut No. 1	0 to 30%
Cut No. 2	30 to 60%
Cut No. 3	60 to 90%

Evaluate the slope of each cut and average boiling point of each cut. Apply the necessary correction.

TBP slope		Av.B.P.		Correction for	
$^\circ\text{C}/\text{percent}$		$^\circ\text{C}$		converting to MAVBP	
Cut No. 1	1.98	166.6		-31°C	ρ
Cut No. 2	0.83	271.0		-16°C	0.769
Cut No. 3	1.20	366.5		-16°C	0.8602
					0.8844

For Cut No. 1 Molal average boiling point = $166.6 - 31 + 273$
 408.6°K

$$K = \frac{\sqrt[3]{408.6}}{0.823 \times 0.769} = 11.71$$

$$\text{Cut No. 2 } K = \frac{\sqrt[3]{528}}{0.823 \times 0.8602} = 11.43$$

$$\text{Cut No. 3 } K = \frac{\sqrt[3]{613.5}}{0.823 \times 0.8844} = 11.67$$

Average K value 11.60

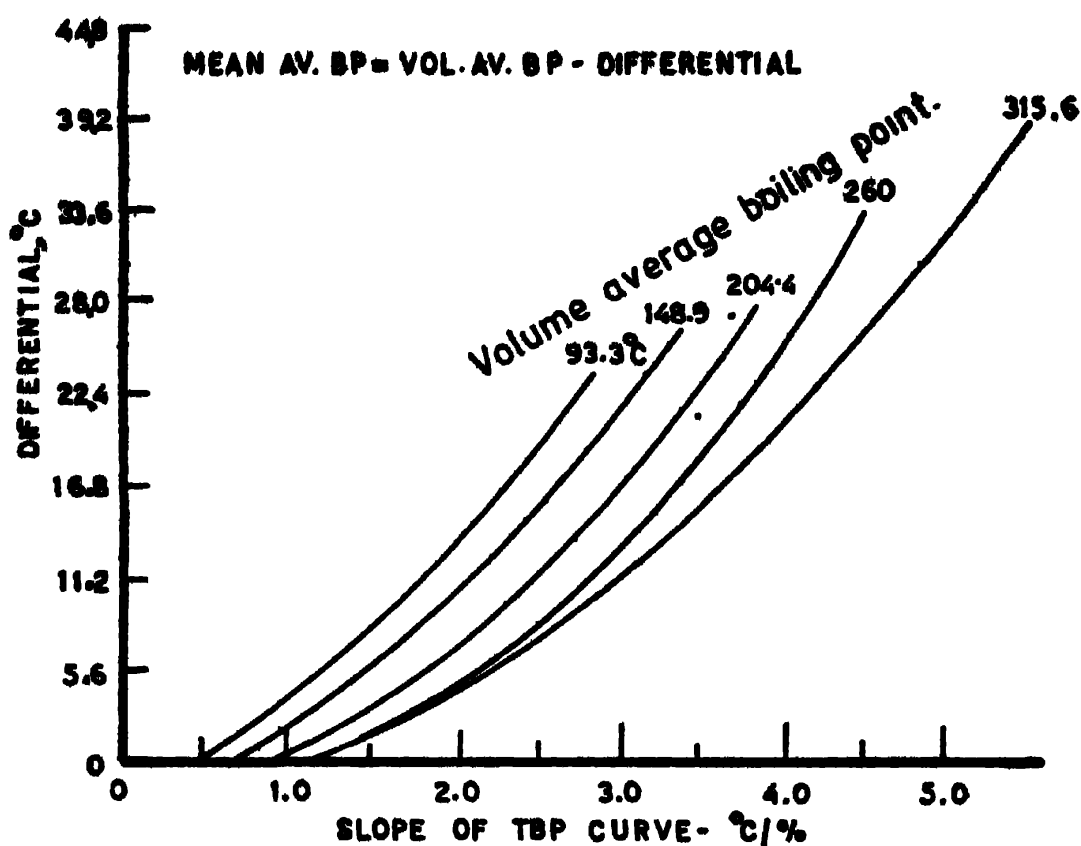
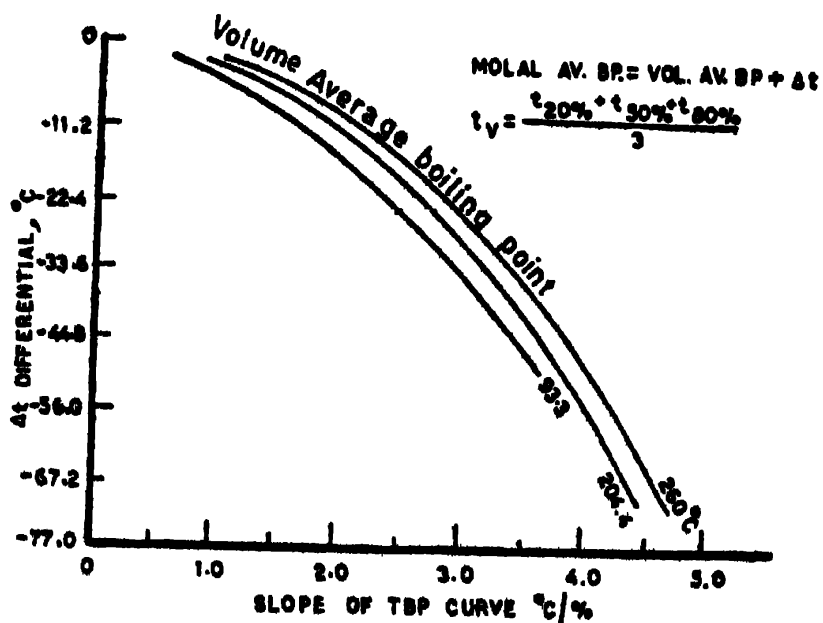


FIG. 2.8(a) Mean average Boiling Point
FIG. 2.8(b) Molal average Boiling Point



(Fig. 2.8(a) and (b) are Reprinted From p. 33
Petroleum Refining
James H. Gary-Glenn, E. Handwerk
Vol. 5 Courtesy of Marcel Dekker Inc, N. Y. 1975

2.2 Thermal Properties of Petroleum Fractions

Some of the important thermal properties of petroleum are discussed in this chapter.

SPECIFIC HEAT

Specific heat of petroleum fraction lies in the range of 0.3 to 0.85 and depends upon temperature and gravity. Lighter fractions have higher values. With increasing density the specific heat decreases. In absence of relevant data, the following correlations can be used.

Bureau of Standards formula⁸

$$\text{Sp. heat} = \frac{1}{\rho} (0.4024 + 0.00081 t) \quad (2.10)$$

where ρ = sp.gravity at 15.6/15.6°C and t = temp. °C.

With API gravity, temperature and characterisation factor (K) (for oils only) the specific heat correlation is given below :

$$\text{Sp. heat}^9 = [0.355 + 1280 (^\circ\text{API}) 10^{-6} + (503 + 1.17 \times ^\circ\text{API}) (32 + 1.8t) 10^{-6}] (0.05K + 0.41) \quad (2.11)$$

where K = characterisation factor ; t = °C

Further, for pure components, the specific heats are listed over a temperature range of 200 to 6000°K by Duran¹⁰ et al.

Watson and Fallon gave the following relation for petroleum vapours¹¹ :

$$\text{Sp.heat} = (0.045 K - 0.233) + (0.44 + 0.01777 K) (1.8t + 32) 10^{-3} - 0.153 \times (1.8t + 32)^2 \times 10^{-6} \quad (2.12)$$

where K : characterisation factor

t .. °C

In processing calculations, the use of specific heat is not immense ; as heat content of the fractions is more versatile and available.¹²

2.2.1 HEAT OF COMBUSTION

Hydrogen is distinct for its heat of combustion i.e. 183.6×10^3 kJ/Kg. Obviously higher hydrogen content fractions will be destined to have more heat of combustion. Thus in the order of paraffins to aromatics, the heat of combustion decreases.

Sherman—Kropff relationship showing heat content with °API is worth mentioning.¹³

$$\text{Heating value kJ/Kg} = 43,434 + 93.2 (\text{API} - 10) \quad (2.13)$$

Gases can be classified by their calorific values. Replacement of one by another is possible as shown by Wobbe number.¹⁴

$$\text{Wobbe No} : \frac{\text{Heat of combustion}}{0.5 \text{ (sp. gravity)}};$$

For different manufactured gases like coal gas, SNG etc. Wobbe No. lies in the range of 21.5 to 38.7

For Natural gas :

Low calorific value	37.1—43.7
High calorific value	43.4—52.4
LPG	72.0—83.5

where

Calorific value is given in K cal/liter and Sp. gravity (Air = 1) in Kg/Cu.M.

Gas modulus is another term conveniently used to replace one gas to another (by increasing the pressure at which it burns).

$$\text{Gas modulus} = \frac{P_1}{\text{Wobbe No.}}$$

An example may be cited here. A manufactured gas of 25 W. No. burning at 1 m. bar can be replaced in a burner with natural gas of W. No. 50.

$$\frac{1}{25} = \frac{P_1}{50}$$

Mfg NG

The natural gas is thus permitted to burn at a pressure 4 times that of manufactured gas.

2.2.2 LATENT HEAT OF VAPORISATION

Latent heat for a fraction varies with the temperature (or pressure) at which vaporisation takes place. This is commonly related to molecular weight, °API and molal average boiling point. Any two of the above parameters are sufficient to give latent heat of vaporization. Latent heat can also be converted from normal boiling point to any other temperature upto critical condition.

The relationship is expressed as

$$L = \gamma L_B \frac{T}{T_B} \quad (2.14)$$

L = latent heat at any temperature (T absolute)

L_B = latent heat at temperature (T_B absolute)

γ = correction factor depends upon reduced temperature.

At the critical conditions, the latent heat vanishes. As the critical temperatures of high API materials are lower than low API materials, the latent heat curves for these materials cross one another.

2.2.2.1. Latent Heat of Fusion

The heat of fusion is approximately fifty per cent of latent heat of vapourisation. For waxy distillates and waxes, the average latent heat of fusion may be taken as 167 to 170 K.J. per kg.

2.2.3 THERMAL EXPANSION

Like all liquids, petroleum fractions also suffer in loss of density due to thermal expansion. Coefficient of expansion is very much required to find out the volume of the container, which is exposed to frequent changes of temperature and this is related to API gravity as given below¹⁵ :

Gravity range API	Mean coefficient of expansion (change in volume for 1°C)
0—14.9	0.00063
15—34.9	0.00072
35—50.9	0.00090
51—63.9	0.00108
64—78.9	0.00126
79—88.9	0.00144
89—93.9	0.00153
94—100	0.00162

2.2.4 SPONTANEOUS IGNITION TEMPERATURES

Definition : The temperature at which a material can catch fire and burn continuously without the aid of external firing

agencies. Paraffins have less ignition temperatures and this precious property is regarded as most useful for the performance of diesel fuels.

Aromatics have high ignition temperatures. In gasoline engines adiabatic compression of the mixture does not raise the temperature to that extent, hence sparking is required for detonation. Gasoline engines this way differ from Diesel engines. Ignition temperature remarkably decreases with increasing molecular weight of the series as well as with the oxygen content of molecule.

Self Ignition temperatures of some Hydrocarbons¹⁶

Paraffins	Temp. °C	In presence of Oxygen	Naphthenes	Temp. °C	In presence of Oxygen
Pentane	418.3	292	Methylcyclohexane	393.3	
Heptane	258.5	284	Methylcyclopentane	468.9	
Decane	252.8	—	Alcohol	551	329
Cetane	235.0	—			
2, 3 Dimethyl hexane	437.8				

Aromatics	Temp. °C	Inpresence of Oxygen
Benzene	651.7	639
Toluene	629.4	
m-Xylene	628.9	
p-Xylene	690.6	
α-Methyl naphthene	565.6	
Decahydronaphthalene	271.1	

Spontaneous ignition temperatures, as determined by Moore,¹⁷ are slightly different from the self ignition temperatures mentioned above. Self ignition temperatures fall with slow oxidation while they increase with the addition of TEL and oxidation inhibitors.

2.2.5 VISCOSITY AND VISCOSITY INDEX

Viscosity is an important property of all lube oils. Lubrication assists in removing the frictional forces between two moving bodies. Viscosity is defined as the forces in dynes required to maintain 1 sq. cm plane, with a unit velocity gradient from another similar plane separated by a distance of 1 cm. The relative viscosity is the ratio of the viscosity to that of water at standard temperature. In all refinery operations instead of absolute viscosity kinematic viscosity is used.

$$\text{Kinematic Viscosity} = \left(\frac{\text{Viscosity absolute}}{\text{Sp. gravity}} \right)$$

All the laboratory viscometers like U-tube, Fenske, Redwood, Engler give kinematic viscosity only. However, Saybolt universal viscometre gives the time in seconds for 60 cc sample efflux, through a standard orifice at the given temperature and is expressed as seconds Saybolt universal (SSU). Engler results are expressed in Engler degrees which gives almost absolute viscosity. Although viscosity is a measurable property of all fractions, it is no way essential for lighter fractions like gasoline, kerosene, naphtha, except for calculating the power consumption in pumping or in atomising purposes.

Lubricants are specified by another derived property namely viscosity index, which indicates the variation characteristics of viscosity with temperature. Dean and Davis had given the following formula¹⁸ :

$$V. I = \frac{I - U}{L - H} \times 100$$

where L = viscosity of a reference oil of zero viscosity in deg. at 37.8°C

H = viscosity of a reference oil of 100 viscosity index at 37.8°C

U = viscosity of test sample at 37.8°C

Viscosity index is explained in the graphical fashion as shown in Fig. 2.9. Two standard liquids L and H are chosen. L is having a V.I of zero and H is having a V.I of 100. The starting viscosity for these samples is known by finding the viscosity of test sample U at 98.9°C. Thus all the three samples have the same viscosity (V) at 98.9°C, but exhibit different viscosities at

37.8°C as L , H and U . By substituting the values in the above equation, the V.I. can be found out. From this relation, it is apparent, that V.I. can be negative or positive or more than 100. L and H can be obtained from standard tables. Commonly paraffinic base oils have high V.I. (100 for reference), conversely naphthene base

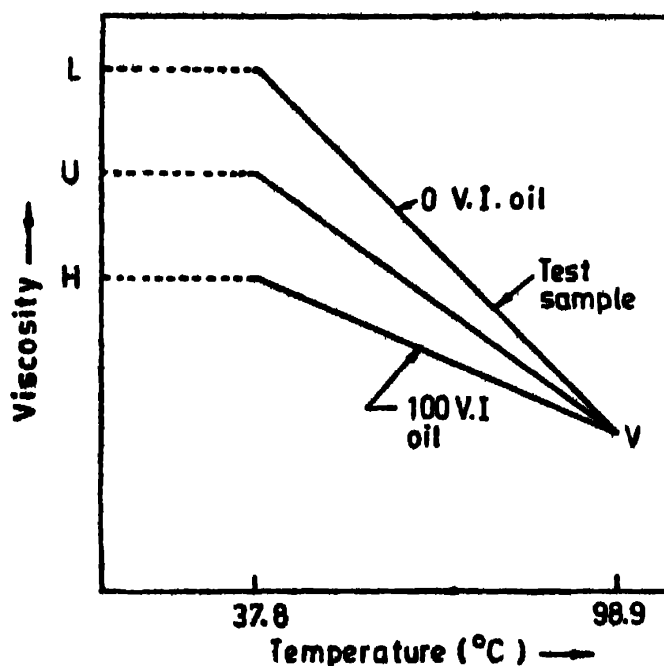


FIG. 29 Viscosity Index—Graphical explanation

oils are given the value 0 (for reference. The higher the V.I. the better is the viscosity-temperatures characteristics. Usually the 100 V.I. oils are good to start at lower temperatures than zero viscosity index oils, of course with low pour points as shown in Table 2.2(a) and (b).

TABLE 2.2(a)
Lowest temperature for easy starting °C

	0 V.I.	40 V.I.	100 V.I.
SAE-20	2.78	-16.6	-23.3
SAE-50	+10	—	- 667

Even in case of diesel fuels, easy starting is related to viscosity and pour point as shown in Table 2.2(b)

Air Temp. °C	Max. viscosity (SUS) at 37.8°C	Max. pour point ° C	Cetane number
-28.9	5.6	-34.4	90
-23.3	7.8	-28.9	83
-12.2	13.9	-17.8	69
- 1.1	21.1	- 6.7	56
15.6	71.1	10.0	36

Viscosity, average boiling point and characterization factor of all the petroleum fractions are interrelated. Any two of these properties can give the other one, as shown in Figs. 2.10(a) and (b).

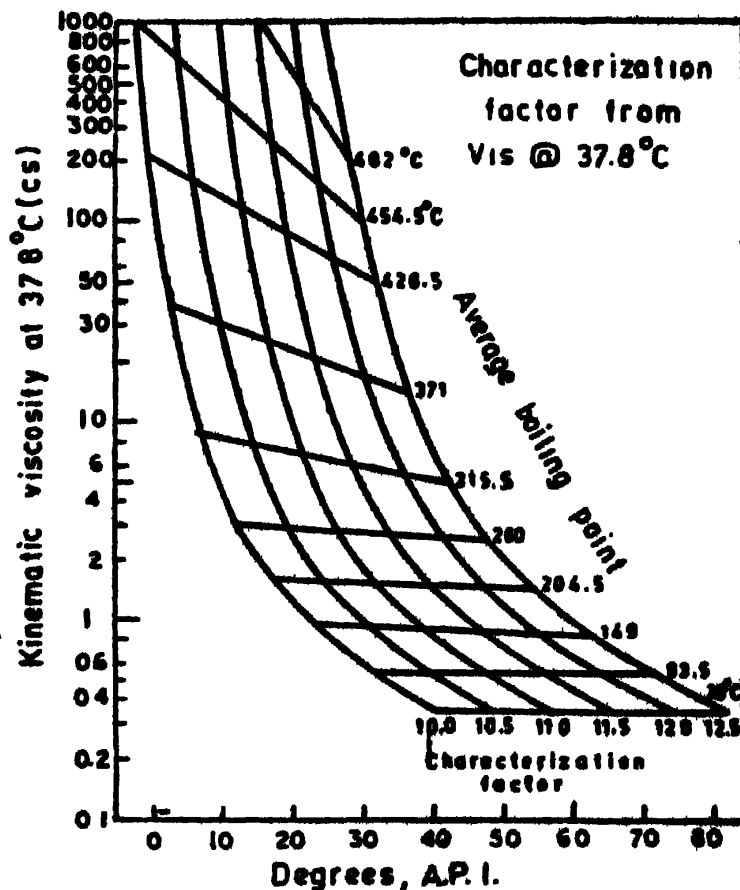


FIG. 2.10(a) Relation between characterisation factor, viscosity at 37.8°C, average boiling point and gravity (API)

(Fig. 2.10(a) & (b) Taken from American Petroleum Refining By H. S. Bell (3rd Edit.)
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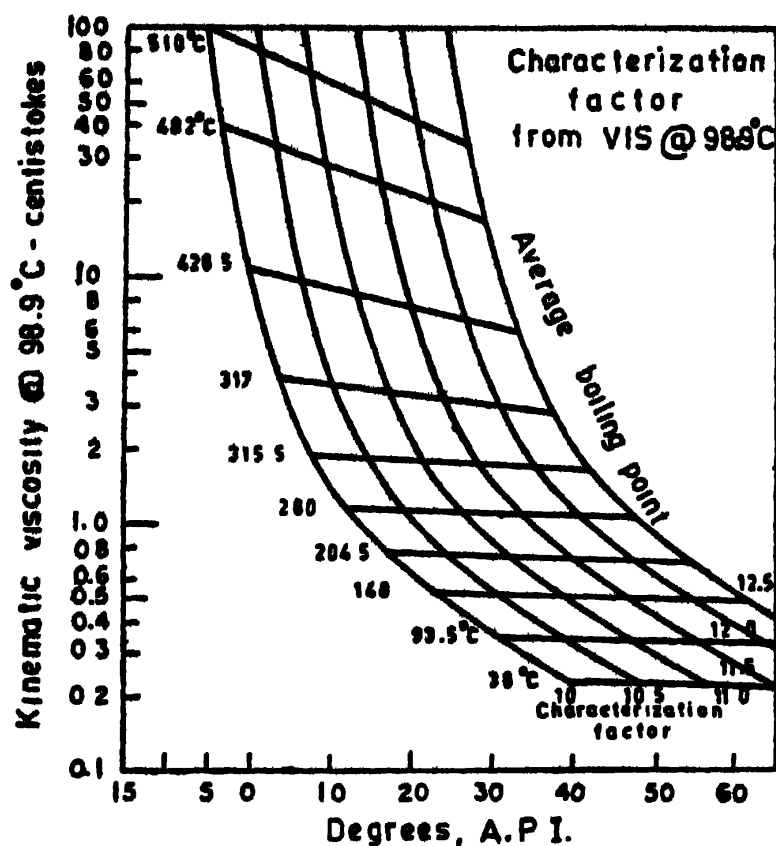


FIG 210(b) Relation between Characterisation factor, viscosity at 98.9°C, average boiling point and gravity (API)

Viscosity is not an additive property, hence it does not follow arithmetic rule, however it can be estimated by extrapolation or interpolation, when represented in ASTM charts. Viscosity at two different temperatures need be available, and is mathematically shown by Walther's equation as given below :

Walther's Equation :

$$\log \log (r+a) = m \log T + b \quad (2.15a)$$

where $T = ^\circ K$

r = centistocks

$a = 0.7$ or 0.8 if $r > 1.5$

m = slope

b = constant

This describes, the viscosity variation characteristics of an oil with temperature. On the basis of this equation ASTM charts were prepared. This is essential specially when the pour point of oil is very high (intrapolation to get viscosity at 37.8°C).

Viscosity of hydrocarbon vapors is related to critical properties by the formula²²

$$M_c = 7.7 \sqrt{M} \frac{P_c^{\frac{1}{3}}}{T_c^{\frac{1}{3}}} \quad (2.15b)$$

M_c = critical viscosity (micropoises)

M is molecular weight

T_c is critical temp. °K and P_c is the critical pressure in atmospheres.

2.2.5.1 Viscosity—Gravity constant

This index of classification connects the viscosity and gravity of the sample by the formula

$$VGC = \frac{10G - 1.0752 \log (V - 38)}{10 - \log (V - 38)} \quad (2.16a)$$

where G is sp.gr. at 15.6°C, V = SSU at 37.8°C

where the measurement of viscosity is not possible at 37.8°C an alternative formula is used.

$$VGC \text{ for heavy oils} = \frac{G - 0.24 - 0.022 \log (V - 355)}{0.755} \quad (2.16b)$$

where V is at 98.9°C

Naphthenic oils have V.G.C, 0.9 and above, while paraffinic oils have 0.8. This is due to specific gravity, which is more for naphthenic oils than paraffinic oils. A nomogram based on the above formula is presented²¹ in Fig. 2.11.

2.2.6 THERMAL CONDUCTIVITY

Much interest was not shown towards this property. Group contribution techniques as developed by Sakiadis and Coates²³ and Bondi²⁴ are helpful in this matter.

Problem 2.6

Raw pressible waxy distillate (A) and dearomatised pressible waxy distillate (B) of Assam Oil Company are having the following kinematic viscosities at 98.9°C and 65.6°C (a) Find the viscosity indices of the two samples, (b) Find the composition of blend which can give a viscosity of 16 CS at 78.9°C

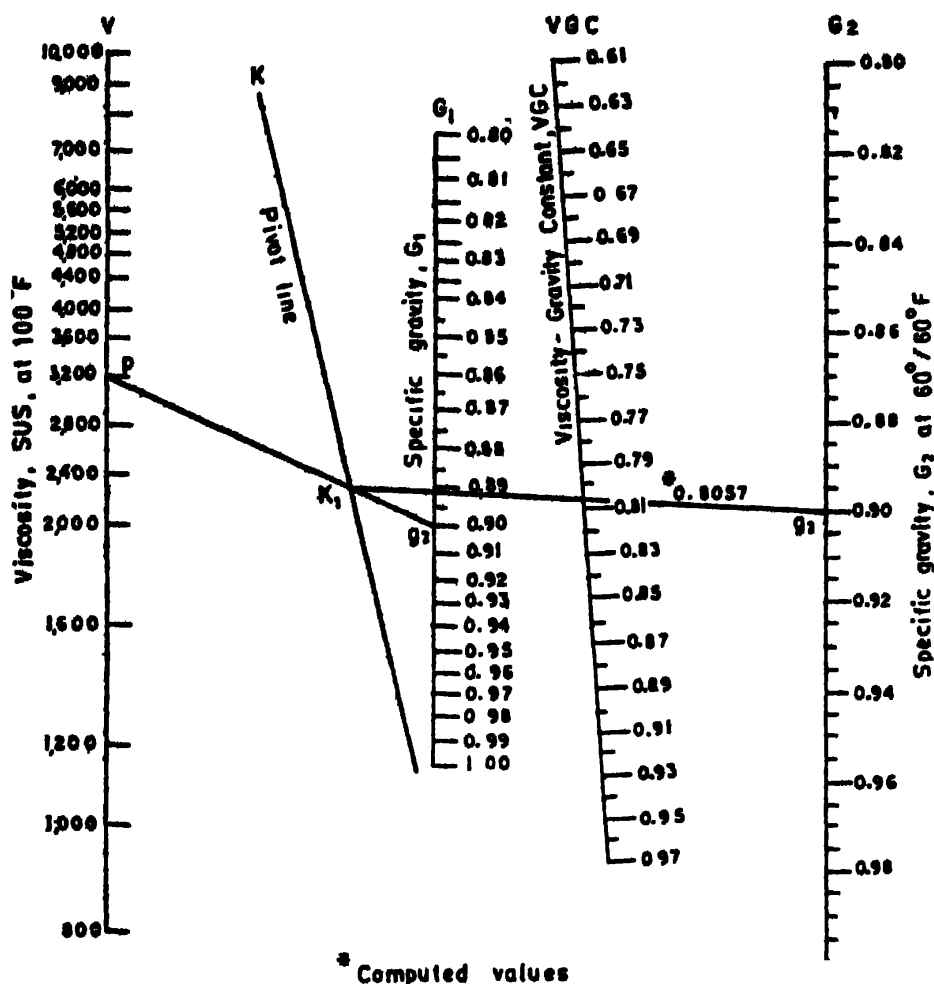


FIG. 2.11 Viscosity Gravity Constant (Graphical Method)

- (a) Raw pressible waxy distillate K.V. at 65.6°C = 24.5 cS
 at 98.9°C = 4.1 cS
 at 65.6°C = 53.5 cS
 at 98.9°C = 7.3 cS
- (b) Dearomatised pressible waxy distillate K.V.

Solution

Refer Fig. 2.12

(a) Plot the above readings on a semi-log graph (ASTM chart). Find the viscosities of the samples at 37.8°C by extension. The viscosities are read as :

For Sample A : 106 cS at 37.8°C

-do- B : 276 cS at 37.8°C

Viscosity Index is calculated by referring to IP tables.

For sample

$$A \quad V. I = \frac{28.06 - 106}{28.06 - 21.40} = -11.70$$

$$B \quad V. I = \frac{91.666 - 276}{91.666 - 55.273} = -5.066$$

Negative viscosity index need not be multiplied by 100.

(b) For this part of the problem, draw a line parallel to x-axis from 16 cs (K.V), so that the line intersects data lines at *P* & *Q*.

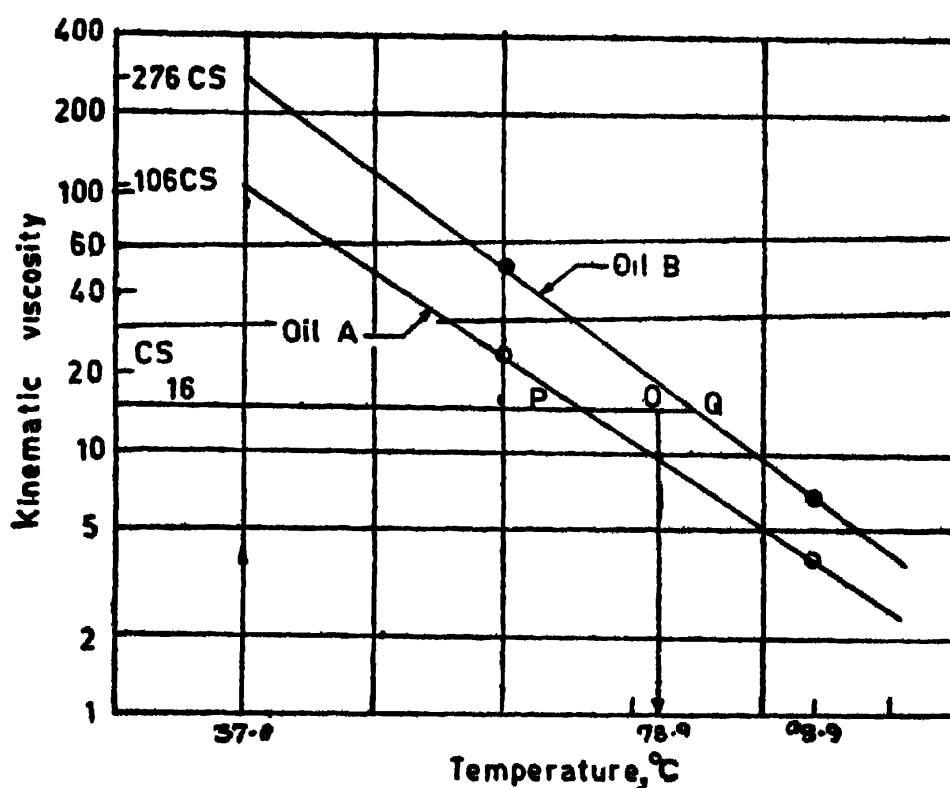


FIG 212 Viscosity of Blends.

Draw a line parallel to y-axis from 78.9°C, such that the line intersects the above at 'O'. Now the blend of 'O' composition will give the required viscosity at 78.9°C

% B in the blend to give

$$\text{the required viscosity} = \frac{PO}{OQ} \times 100 = \frac{1.5}{2.2} \times 100 = 68\%$$

at 78.9°C

further viscosity at 37.8°C can be calculated by the correlation given by R.E. Hersh et al¹⁹.

$$KV_{87.8} = 2.808 \left[KV_{99.6} - \frac{0.5}{KV_{99.6}^{1.38}} \right]^{1.05} \text{ for paraffinic oils}$$

$$KV_{87.8} = 2.45 \left[KV_{99.6} - \frac{0.213}{KV_{99.6}^{1.08}} \right]^{1.8} \text{ for naphthenic oils}$$

Viscosity can be determined by different instruments and different methods and all can be converted to SSU or centi Stokes (Table 2.3)

Porter developed a method to find the viscosity of a component at different temperatures by a plot similar to Duhring's. According to this plot the viscosities of a test liquid at different temperatures are plotted with reference to a temperature—viscosity variation curve for a reference liquid. It follows that the viscosities of a test sample and reference liquid will be same at definite temperatures of these two. This is shown in Fig. 2.13.

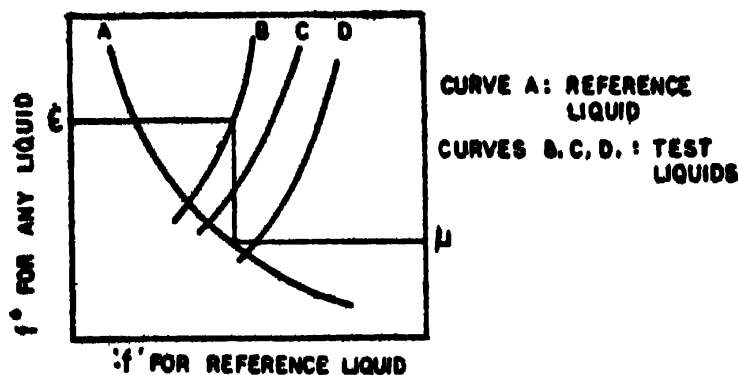


FIG. 2.13 Viscosity determination.
By Porter's Method.

To get the viscosity of a test liquid at $t^{\circ}\text{C}$ one has to proceed horizontally till the corresponding curve is reached and then run down vertically to meet the reference curve; horizontal reading on viscosity scale at the point will give the viscosity of test liquid.

Viscosity of pure components can be estimated by Souder's²⁰ method.

$$\log (\log 10 \mu) = \frac{1}{M} p - 2.9 \quad (2.18)$$

TABLE 2.3 CONVERSION OF VISCOSITY

Centi Stoke	Engler degrees	Saybolt Seconds at 54.44°C	Red wood Seconds at 60 °C
2.0	1.140	32.66	30.95
2.5	1.182	34.46	32.20
3.0	1.124	36.07	33.45
3.5	1.266	37.67	34.70
4.0	1.308	39.17	35.95
4.5	1.350	40.78	37.20
5.0	1.400	42.48	38.45
5.5	1.441	43.98	39.80
6.0	1.481	45.59	41.05
6.5	1.521	47.19	42.40
7.0	1.563	48.79	43.70
7.5	1.605	50.44	45.00
8.0	1.653	52.10	46.35
8.5	1.700	53.80	47.75
9.0	1.746	55.51	49.10
9.5	1.791	57.21	50.55
10.0	1.837	58.91	52.00
12.0	2.020	66.03	58.10
14.0	2.219	73.54	64.55
16.0	2.434	81.25	71.40
18.0	2.644	89.37	78.45
20.0	2.870	97.69	85.75
25.0	3.455	119.10	104.70
30.0	4.070	141.20	124.40
35.0	4.695	163.5	144.2
40.0	5.355	186.0	164.3

where I is a parameter give for different liquids

M = molecular weight

ρ = specific gravity at $t^\circ\text{C}$

μ = viscosity in CPs. at $t^\circ\text{C}$

I in Souder's equation is calculated from the group contributions as given below :

Atom	H	O	C	N	Cl	Br	I
Contribution	+2.7	+29.7	+50.2	+37	+60	+79	+110
Double bond			-15.5				
5 member ring			-24				
6 member ring			-21				
Side groups of 6 member rings							
For components of molecular weight less than 17							-9
For components of molecular weight greater than 17							-17
ortho, para positions							+3
meta position							-1
OH	+57.1						
NO ₂	+80						
		C=O					+90

Problem 2.7

Estimate the viscosity of phenol at 80°C ($\rho = 0.9692$)

Solution

For 5 H atoms		5×2.7	13.5
6 Carbon atoms		6×50.2	301.2
OH			+57.1
Ortho position			+ 3
Mol. wt.	= 94		374.8
For one six ring			= -21
3 double bonds		(-15.5×3)	= -46.5
one side group mol. wt greater than 17			= -17.0
			<u>- 84.5</u>

$$I = 374.8 - 84.5 = 290.3$$

$$\log [\text{Log } 10 \mu] = \frac{290.3}{94} \times 0.9692 - 2.9$$

$$= 2.991 - 2.9 = 0.091$$

$$\mu = 1.7 \text{ cps. at } 80^\circ\text{C}$$

Thomas method is based up on reduced temperature and is given by the relation²⁰

$$\log \frac{8.569\mu}{\rho^{0.5}} = \theta \left[\frac{1}{T_r} - 1 \right] \quad (2.19)$$

where T_r is reduced temperature

θ = smoothing group coefficient

Smoothing group (atoms)	Contribution
C	-0.426
H	+0.249
O	+0.054
Cl	+0.340
Br	+0.326
I	+0.335
Double bonds	+0.478
C_6H_6	+0.385
S	+0.043
CO	+0.105
CN	+0.381

Problem 2.8

Estimate the viscosity of benzene, given

Specific gravity (ρ) = 0.875 at 20°C ; T_c (critical temp.)
= 562° .1 K

Solution :

For 6 carbon atoms $6 \times -0.426 = -2.556$

For 3 double bonds $3 \times 0.478 = 1.434$

For 6 H atoms $6 \times 0.249 = \frac{1.494}{2.928}$

$= 2.928 - 2.556 = 0.372$

$= 237 \times 0.917 = 0.8715$

$$\log \frac{8.569}{(0.875)^{0.5}} = 0.372 \left[\frac{562.1}{293} - 1 \right]$$

$\mu = 0.87 \text{ CPS at } 20^\circ\text{C}$

2.2.7 Thermoviscosity

This is given by following relations :

Thermoviscosity = $15 + 148 \times \text{kinematic viscosity}$ or

Thermoviscosity = $46 \text{ SSU} - 1,183$ where SSU is determined at $15^\circ.6\text{C}$

Thermoviscosity is not of much importance, however for fractions having less viscosity, the expression looks to be convincing. Industrially, thermoviscosity is important for illuminating oils. Frequently thermoviscosity is expressed in terms of Ring number given as

$$\text{Ring No. : } \frac{\text{Thermoviscosity}}{5} - 10(46 - \text{API}) \quad (2.20)$$

Usual ring number for most of the illuminating oils is in the range of 60 to 130.

2.3. Important products-properties & Test methods

Distillation of crude yields number of cuts of varying boiling ranges. These fractions or cuts are processed suitable to utility when they are known as products. In the order of increasing boiling points, the main fractions from distillation of crude, are

Gas/light-naptha/gasoline	Solvents/Fuels/motor spirits, etc.
Kerosenes (light distillates)	Jet fuels/illuminating oils/heating oils
Gas oils or middle distillates	Diesel fuels, cat-cracking oils, etc.
Heavy distillates	Lubes/Waxes/fuel oils, etc.
Residuums	Asphalt, Bitumen etc.

2.3.1 GAS

Gas from petroleum is classified under several names like natural gas, associated gas, dissolved gas, casing head gas and off gas from refinery.

2.3.1.1 Natural gas

Its name indicates that it is readily available in nature, in almost as a finished product. It contains mainly varying proportions of methane. It may be accompanied by other dry gas

fractions like ethane and propane to a small extent. In addition to these combustibles some inerts like CO_2 , N_2 , noble gases are also present. The proportion of methane ranges from 85% and goes upto 98%.

2.3.1.2 *Associated gas*

This is obtained from oil reservoirs and this exists as a separate gas cap over liquid phase. Though the gas mainly consists of methane and to some extent ethane and propane, the proportions vary depending upon the reservoir conditions. When the gas phase is taken out, it may still contain some liquid hydrocarbons mainly of volatile range like butane and pentane, which when condensed are termed as natural gasolines.

2.3.1.3 *Dissolved gas*

Gas may be present in the liquid hydrocarbons mainly in the dissolved state depending upon the formation pressure. When the pressure is decreased, this dissolved gas comes out of the oil. Gas production upto 10% crude produced is not uncommon with the oil reservoirs.

It is fair to strip off such dissolved gas before crude is transported to long distances by means of pipe lines or tankers. The remaining dissolved gas is first to come out of the distillation column because of higher temperature than the surroundings.

2.3.1.4 *Casing Head gas*

Gas that has escaped through oil well christmas trees is termed as casing head gas. It is also more or less similar to natural gas but contains less % of methane and high percentage of ethane and propane than natural gas. It is a by-product of oil production

2.3.1.5 *Refinery off gas*

In a refinery, gas is formed in cracking and reforming operations due to the thermal degradation of liquid hydrocarbons. During stabilisation of wild gasolines or processed gasolines, the gases are vented. Thus the gas is mainly a mixture of saturates and unsaturates and quantity is also not assessible. This forms

a major source of heat energy for refinery, as well as feed stock for petrochemicals. In fact, without any exclusion, all these gases can be utilised for petrochemical industries.

All the gases contain impurities like CO_2 , N_2 , mercaptans, H_2S , water vapour, suspended impurities etc. First three paraffins are gases at room temperature. Mixture of methane and ethane is called dry gas, while propane-butane mixture is called wet gas. Where petrochemical industries are not instituted dry gas would find its use mainly in the refinery fuel system. Wet gas is usually liquified and sold for commercial purposes. Butane is diverted to gasoline streams as a blending component, as butane has more commercial value when blended with gasoline.

2.3.1.6 *Liquified petroleum gas (LPG)*

The gas that is vented from refinery distillation units, is processed and conveniently stored after liquefaction. For domestic heating purposes, it is supplied in small cylinders 15 kg or 12 kg), while for industries tanker supplies are called in. This gas is known as liquified petroleum gas as it is stored in vapor liquid mixture. Ease of handling, smokelessness, good and steady heating rates are some key points, that made this fuel a popular kitchen aid to the housewife of modern times. Rising demands of this fuel in domestic and industrial circles are met by the refinery by installing processing units.

Different types of mixtures resulting from propane-butane blends are sold as LPG. Infact propane itself can be utilised for this purpose and hence the dearth of availability of butane does not deter the manufacturers.

Most important property of this fuel mixture is vapour pressure. These fuels are graded according to vapour pressure and temperature at which 90% or 95% is evaporated. LPG is produced in many grades as listed below :

1. Predominantly butanes
2. Butane—propane mixtures, mainly butanes
3. Butane—propane mixture (equal volumes)
4. Less butane—propane mixture
5. Butane—propane mixture (more propane)
6. Predominantly propane

2.3.1.7 *Important Tests*

Vapour pressure of the sample is foremost important. This is found out by Reid's—Vapor pressure apparatus (See Fig. 2.14). The test is described in gasoline testing. Characteristic vapor pressure²⁵ of these mixtures at 38°C varies from 5 to 13 kg/cm². 95% evaporation point at 760 mm Hg shall be kept less than 0°C. In tropical regions, a fair amount of butane may be mixed so that 95% evaporation point shall be around 0°C.

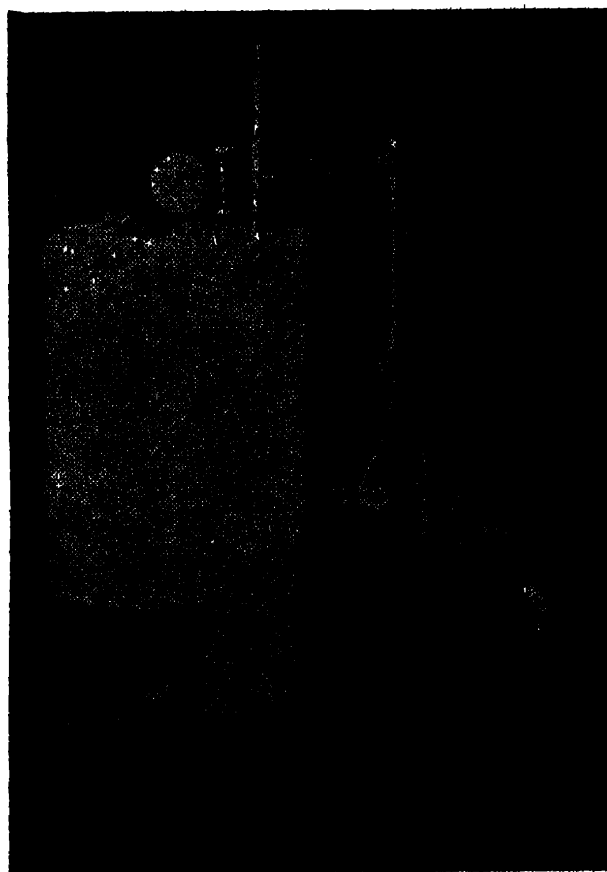


FIG. 2.14 LPG Testing (Reidvapor Pressure)

Natural Gas Processing Supplies Association (NGPSA), standards elucidates tests, properties and methods for handling such mixtures. While storing these gases, hydrocarbon dew point is reduced to such a level that condensation by releasing the pressure cannot be experienced. In addition to satisfactory vapor pressure and evaporation point, the gas should be free from corrosive compounds. Hydrogen sulfide, Carbonyl sulfide

are such contaminants which are kept below 5 to 6 grains per 10 cubic meters; further it should also be free from moisture. Usual gross calorific value is in the order of 38 to 82 MJ/M³. For facilitating leak detection, the gas is mixed with small amounts of odourous mercaptans.

A typical LPG composition of an Indian Refinery is given below :

LPG (Butane-propane mixtures)	
Vapour pressure at 65°C	= 10 to 26 kg/cm ²
Vapour pressure at 38°C ± 0.1	= 6.7 kg/cm ²
95% evaporation temperature	= -2°C
Sulfur % by weight	-0.02
H ₂ S	- Nil
Moisture	- Nil
<i>Composition</i>	
Ethane	- traces
Propane	-24.7%
i-butane	-36.7%
Butane	-38.5%
Pentane	- Nil

L.P.G. being a manufactured gas its composition remains same. In the case of natural gas the composition varies from mine to mine, even in the same mine from time to time.

2.3.2 GASOLINE

Naphtha or Gasoline (petrol as is known in India) is the next fraction to follow gas. This is a volatile fraction and is known as motor spirit. The boiling point ranges from 37°C to 180°C. Gasoline is a finished product, while raw fraction is termed as naphtha or light boiling fraction. There are different types of gasolines produced by the refineries (approx. 40 types) and almost 90% of the product is exclusively consumed by automobile industry and the rest by aviation industry. Most refineries produce two primary grades, regular and premium both either leaded or unleaded. The product is so important that the integration of refineries has become a reality to produce as much as 60-70% of gasoline from crude, especially in countries like U.S.A.

Gasolines are never analysed for individual components, yet

around 1500 compounds were isolated just for academic interest. Light straight run gasoline (LSR) consists of C_5 to 90°C fraction. This is the fraction which cannot be reformed for improvement in octane number. This cut as such contributes good octane number (with high susceptibility to lead) and bears light end distillation characteristics of gasoline. LSR is also known by the name virgin gasoline and does not have desired qualities or properties suitable for usage in automobile industry.

Hence straight run gasolines are blended with the processed gasolines obtained by various methods, these are :

1. Reformate gasolines,
2. Coker gasolines,
3. Alkylated gasolines,
4. Polymer gasolines,
5. Cracked gasolines and
6. Hydrocracked gasolines.

2.3.2.1 Tests for Gasoline

The important tests prescribed for gasolines are :

1. ASTM distillation,
2. Reid vapor pressure,
3. Octane number,
4. Gum content,
5. Sulfur content, etc.

ASTM DISTILLATION (15 : 1448—P : 18, ASTMD—86)

In this test 100 ml of sample is distilled in a standard flask at a uniform rate of 5 cc per minute. The distillate is condensed in a brass tube condenser, surrounded by a water bath kept at 0°C by ice-water mixture. First drop from the condenser must be available in 5 to 10 minutes after heating started, at which the recorded temperature is mentioned as initial boiling point (IBP) of the sample. The vapor temperature is recorded at each successive 10 cc distillate collected in a measuring cylinder. The test continues in the same way till 95% of fraction is condensed. At this juncture, the heat intensity may be increased to obtain the maximum boiling point also known as end point (EP) (See Fig. 2.15)

Fluctuation in temperatures is common when last two or three ccs of sample are distilled. When the bottom of the flask

shows dryness, the temperature recorded corresponds to final boiling point. The distillate collected shall not be less than 98% and the difference is accounted as loss ; usually ascribed to light

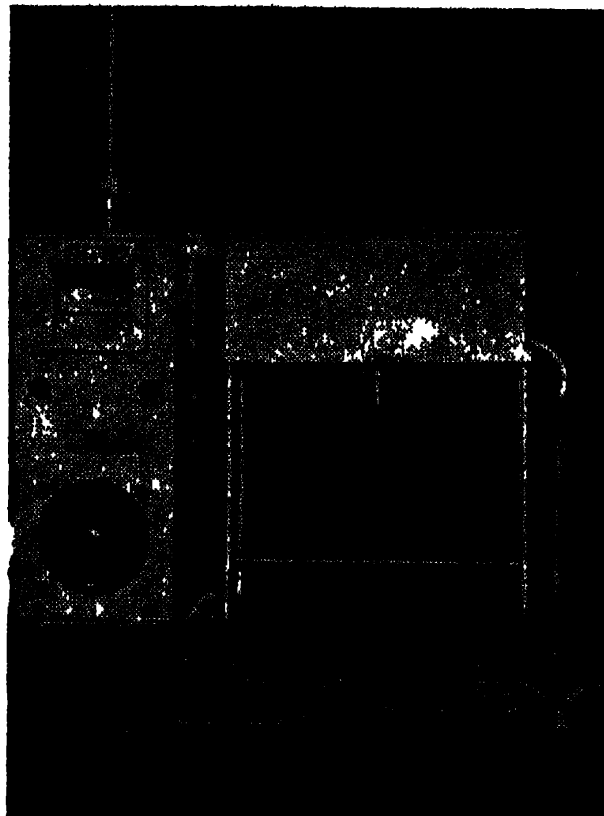


FIG. 215 ASTM Distillation

ends. This method of distillation is followed for most of the product specifications. When middle distillate like diessels are to be tested, instead of 100 ml. sample, a 200 ml. sample is taken. Similar adjustment of heating rates are followed to obtain IBP in 10 to 15 minutes time. This test is conducted with standard equipment only. The boiling points in this method need not be adjusted to 760 mm pressure ; although it is preferred at times of dispute. ASTM distillation specifies the evaporation characteristics of gasoline. Accordingly gasolines fall mainly into 3 types : Type A, Type B and Type C. In all these types 10%, 50% and 90% boiling point along with IBP and FBP are mentioned.

Ease of starting is governed by IBP to 10% range boiling point. Lower IBPs are preferred for cold climates. A drawback of very low IBP is vapour locking of the engine due to high

TABLE 2.4

RELATIVE EQUILIBRIUM VOLATILITY LOSSES OF GASOLINE OF RVP : (0.6 kg/cm²)

Sl. No.	Relative losses at 38°C (b) (Sea level)	Altitude (Meters)	Atmospheric pressure (a) N/sq.m ²	Temp. °C	Losses at altitude and ambient temp.
1	2.55	1,800	81,000	3	2.22
2	3.63	4,600	57,000	-14.7	3.02
3	6.27	8,500	33,000	-40	4.64
4	13.79	14,000	15,000	-50	10.12

(a) Ernest E. Ludwig, *Applied Process Design for Chemical and Petrochemical plants (GPC)*.

(b) Taken loss at sea level and 30°C as 1%.

evaporation. This has been to some extent been alleviated by fixing vapour pressure, which is furnished by entire boiling stock. Further, evaporation losses can also be related to vapour pressure. When gasoline tanks are filled up, the vapour that occupied the tank has to be displaced and losses due to such kind of phenomenon are called 'breathing losses' which are inevitable in all filling operations. Breathing losses are in addition to evaporation losses due to ambient temperatures. (Table. 2.4) with all these considerations, to ease starting, winter gasolines and summer gasolines are produced to satisfy the seasonal specifications. Rate of acceleration follows after the starting operation which is best judged by the mid region boiling range (say 30-60%). Rapid warmup is not very essential. It is generally influenced by prevailing weather conditions. Warmup period is defined as the time required to develop fully the engine power. Usual running of engine to 6-8 Km, should be a well considered warm up period and this is closely governed by % distilled at 70°C, with reference²⁶ to minimum ambient temperature as shown below :

% Distilled at 70°C	3	11	19	28	38	53
Minimum ambient temp. in °C	26.7	15.6	4.4	6.7	-17.8	-29

This explains that 11% should be distilled at 70°C, if the ambient temperature is 15.6°C, for maintaining the required warm up. Evaporation losses and vapour locking are guided by RVP and ambient temperatures, as shown below :

Ambient Temp., °C	15.6	21.1	26.7	32.2	37.8	43.3	48.9
Max. RVP (lbs/in ²)	12.7	11.0	9.4	8.0	7.0	6.0	5.3
(kgs/cm ²)	0.879	0.782	0.66	0.56	0.496	0.423	0.38

ASTM distillation curve closely reveals the following :

If 10% boiling point is low ; then

Flash point,	— low
Ease of starting,	— excellent
Vapour losses,	— very high
Vapour locking,	— high

30-60% boiling point range gives information on

- (a) Warm up period (b) Good evaporation

If the range of boiling point is high gasoline will not be evaporating normally. If 90% boiling is high, then crank case dilution also increases as the fuel is not volatile at the working conditions of carburettor (Fig. 2.16).

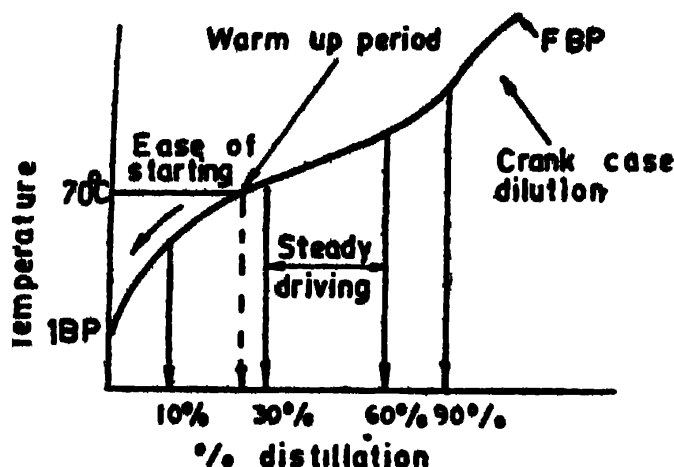


FIG 2.16 ASTM Distillation Characteristics

2.3.2.2 Reid Vapour Pressure (IS : 1448-39)

Vapour pressure of all volatile fractions is measured by the above apparatus at $(38^{\circ} \pm 0.1^{\circ}\text{C})$. The apparatus consists of two chambers. The lower chamber is in the form of cylindrical bomb for holding the test sample. Above this, there is air chamber which is a hollow cylindrical space, designed to possess four times the bomb volume. The top portion of the chamber is fitted with a bourdon gauge for pressure indication. For the test, the bomb is first filled with the sample up to the brim and immediately the valve is closed and connected to the air chamber. The apparatus is now immersed in a water bath kept at $38^{\circ} \pm 0.1^{\circ}\text{C}$. The maximum pressure indicated by the gauge is counted as the Reid vapour pressure of the sample. LPG, gasoline, naphthas, jet fuels are tested like this. It is found that true vapour pressure in most of the cases is higher than the indicated RVP, and the variation for different fractions is different. Maximum difference is indicated in case of crude oils. Relative expression 'True vapour

pressure to RVP' is also sometimes indicated and for gasolines it is in the range of 1.03 to 1.45, while for crudes it goes upto 10.

During testing, the following correction is applied for accommodating the changes in water vapour pressure corresponding to temperature variation from air to bath temperature.

$$\text{Correction : } \frac{(P_a - P_s)(t - T)}{T \cdot K} - (P_T - P_s)$$

where, P_a —atmos. pressure, P_s —vapour pressure of water at $t^\circ K$, t —air temp. $^\circ K$, T —Temp. at which test is done $^\circ K$, P_T —vapour pressure of water at $T^\circ K$.

Volatility tests are intended for smooth performance of engine under all weather. The importance can be judged by U.S. Volatility.

TABLE 25
U. S VOLATILITY TRENDS OF GASOLINE

	Regular				Premium			
	Winter 1956—1966		Summer 1956—1966		Winter 1956—1966		Summer 1956—1966	
Reid vapour pressure	0 773	0 822	0 605	0 633	0 773	0 836	0 619	0 639
10% Evaporation Temp $^\circ C$	47 3	43 3	53 9	51 7	46 8	43 3	53 3	51.7
50% Evaporation Temp $^\circ C$	100	93 3	104	97 9	98 4	98 9	103 6	102

2.3.2.3 Octane Number

Octane number is defined as percentage volume of *i*-octane (2, 2, 4-trimethyl pentane) in a mixture of *i*-octane and *n*-heptane that gives the same knocking characteristics as the fuel under consideration. Knocking is due to untimely burning of fuel in a spark ignition engine, which results in loss of power and sometimes it is powerful enough to cause damage to engine parts. With the advent of petrol engines of high compression ratios the tendency of knocking has also increased. Knocking

is mainly due to two reasons, one assigned to engine and the other to fuel. The fuel part is only dealt here. Being a blend, gasoline responds in different ways, even in the same engine, depending upon the components present. Iso-paraffins and aromatics have high octane numbers while *n*-paraffins have very low value (heptane 0), unsaturates do have high octane values but not preferred due to gum contribution. Naphthenes usually lie in between *i*-paraffins and aromatics. Even among *n*-paraffins also the octane number of the lower carbon series is very high (methane has 104) and that is the reason why natural gasolines or LSR (C_5 -100°C) have high octane ratings. Octane number is influenced by different factors like speed of the engine, ambient weather conditions, altitude, combustion chamber deposits and coolant temperature.

Knock rating is tested by CFR Engine for different purposes and the conditions of test are furnished below.

Method	Research	Motor	Aviation	Aviation supercharge
Designation CFR	F ₁	F ₂	F ₃	F ₄
Engine rpm	600±6	900±9	1200±12	1800±45
Air intake °C	75±1	38±1.4	75±2	75±2
Coolant temp. °C	100±1.5	100±1.5	140±5	140±2

Motor method (P. 26, ASTM D357-58) gives the octane rating of high way driving (high speeds), while research method (P. 27, D 908-58) gives for city driving (low speed) conditions F₁ & F₄ methods are for aviation gasolines.

Some additives like tetraethyl or methyl lead are extensively blended into gasolines to boost the octane number.

Octane number estimation for leaded gasolines was furnished by McCoy²⁷ as

$$\text{Octane number} = A(\% \text{ aromatics in fuel}) + B$$

where A & B are constants.

After analysing vast data, the above relation was formulated. The octane number variation with aromatics resulted in a straight line and A and B are the slope and intercept of such a line.

Ambient conditions—Octanes²⁸ number :

Any engine during service has to encounter different weather

conditions. For smooth running it is better to adjust the octane rating of the fuel under such circumstances.

Altitude : With increasing altitude a fuel of less octane value is satisfactory. For every 100 meters increase in altitude drop of one unit RON in fuel quality is allowed.

Humidity

The performance of the engine is again responsive to humidity conditions. Engine working on high humidity conditions require less octane fuel. For an increase of 10% humidity at 25°C a drop of 0.5 RON in fuel quality is permitted.

Engine Speed

High speed engines require low octane value fuel. For an increase of 300 RPM in an engine speed, a decrease of one unit RON of fuel quality is permissible.

Air temperature

Cold countries require less RON fuel than hot countries. With a rise of 12°C in air temperature, an increase of one RON in fuel is required to compensate the effect of air intake temperature.

Coolant temperature

For every 6°C increase in coolant temperature, the engine demands an increase of one RON in quality of fuel as essential. By this one can judge the importance of coolant.

Spark advance

This is purely a mechanical adjustment requiring 1.5 RON increase for 1° advancement of sparking.

Combustion chamber deposits

Running of an engine over sufficiently long periods, invariably results in deposits. It is essential to increase the octane number of fuel by one unit for 5000—10000 km of running.

Alkylated gasolines and reformed (catalytic) gasolines have high octane numbers. While polymer gasolines contribute to medium extent (60-80) RON, gasolines produced by cracking and hydrocracking techniques yield about 60 RON. The light ends of any gasoline produced by thermal decomposition of higher

stocks give good value RON, still they are not preferred because of the large quantities of unsaturates.

2.3.2.4 *Oxidation—Stability (Gum content)*

Motor gasolines are often stored for six months or even longer before use. So it is essential that they should not undergo any deleterious change under storage conditions. Further gasolines should remain free from deposits during discharge from the fuel tank of a vehicle to the cylinder of its engine, otherwise these harmful deposits are built up in the tank, fuel lines and in valves and cause extensive choking. Gasoline manufactured by cracking processes contain unsaturated components which may oxidise during storage and form undesirable oxidation products. An unstable gasoline undergoes oxidation and polymerisation under favourable ambient conditions, forming gum, a resinous material. This in early stages of formation may remain in solution with gasoline but due to further chemical changes may be precipitated.

Gum formation appears to be the result of a chain reaction initiated by radicals such as peroxides and catalysed by the presence of metals, particularly copper, which might have been picked up during refining and handling operations.

This deterioration of gasoline can be eliminated for a substantial period of time by addition of small quantities of antioxidant additives known as inhibitors. Inhibitors retard the oxidation of the olefin constituents of the fuel. Some such inhibitors are normally phenols or amine compounds, and small quantities between 0.001 and 0.02 percent by weight are usually sufficient to ensure good stability.

Gum is of two kinds, one is known as existent-gum (pre-formed) while the other is called potential gum (ultimate). These two gums are estimated by two different methods. Existent gum, as already available in solution, is to be separated by evaporation of the volatile gasoline. This is estimated by ASTM D381; IP 131 test. In this test, a sample of 100 ml. is evaporated with the aid of a heated jet of air, while the sample is maintained at 160-166°C. After the evaporation of the sample the residue is weighed. Usually gum content should not exceed 6-10 milligrams per 100 ml. of gasoline.

Potential or ultimate gum content of the gasoline is evolved by oxidising the sample with oxygen under restricted conditions, thus assessing possible gum formation during storage.

Induction period for gum formation is estimated by Bomb method (ASTM D525 ; IP 40 : P. 28). This employs an atmosphere of oxygen at initial pressure of (7 kg/cm²) over the test sample of 100 ml. in a specially designed bomb. The bomb is fitted with a pressure gauge for indication of pressure, another connection is provided for feeding oxygen. The bomb and its contents are kept in a water bath and heated continuously at 100°C till the test is over. Due to slow oxidation gum formation begins and the pressure of oxygen in the bomb slowly falls. The time required for fall in pressure by 0.15 kg/cm² within fifteen minutes is taken as break point. The difference in time from placement of the bomb to break point is the required induction period. More induction period means more the stability of gasoline, hence less chance of gum formation. A minimum figure of 240 minutes usually ensures satisfactory limit for storage. Induction period in hours is equivalent to months that the gasoline can be stored under commercial terms. Further, extent of inhibitor (additives) to be added is guided mainly by induction period.

2.3.2.5 Sulfur

In addition to corrosiveness and pollution, sulfur compounds are extremely harmful to the susceptibility of gasolines to tetra ethyl lead (TEL).^{29a} More TEL is required if sulfur components are present in gasolines. The effect of overcoming sulfur compounds is done by adding more ^{30, 31} lead. The effect of sulfur on lead can be predicted by the relation given as :

$$L = \frac{a_0 - a}{a_0} \times 100$$

where, a_0 = TEL present in gasoline with sulfur compounds

a = TEL present in gasoline, free of sulfur compounds,

L = % TEL excess required to boost the octane number of sour gasoline to the same extent as sweet gasoline.

Sulfur is also termed as noncorrosive sulfur, provided the sulfur exists in alkyl disulfide form only. Most of the sulfur in

crude is concentrated in heavier fractions, lighter fractions require relatively less cumbersome treatment techniques. Total sulfur is estimated by bomb method (1 P. 6/60, P. 33) or lamp method (P : 34) and mercaptan sulfur as silvermercaptide (P. 36 : IP 104/53).

2.3.3 ADDITIVES FOR GASOLINE

While modern gasoline engines have been designed for efficient use of gasoline, still, gasoline engine operation is not entirely trouble free. Complete combustion of gasoline in engine is rare. Motor oils used for lubrication cause deposits in the combustion chamber. These deposits (presumably of high carbon ring compounds) enter the crank case of the engine to form lubricating oil sludges along with unburnt gasoline. Other source of trouble is effluent through positive crank case ventilation which causes deposits in the delivery end of the carburettor. Thus a clean combustion is remote ; hence additives are preferred to reduce the deposits as well as pollution belches. The effect of sulfur in different forms on lead requirement is presented in Figs. 2.17a & b, c & d.

Different types of additives are blended into gasoline, in fact in all petroleum fractions, to give uninterrupted and smooth service. Additives for different functions are classified as follows :

1. Anti-icings and detergents
2. Inhibitors for (a) corrosion (b) oxidation
3. Combustion aids
4. Anti-knocks
5. Colours and dyes.

2.3.3.1 *Anti-icings and detergents*

During cold and wet weather, spark ignition engine has a tendency to stall till the combustion chamber is fairly warmed up. Formation of ice crystals begins when the ambient temperature is -5 to 10°C , at a relative humidity of 65%. This phenomenon is observed even when gasoline is free of moisture, so, obviously moisture is contributed by air. During vaporisation of fuel in carburettor, there is evidently a good temperature drop. These two facts result in uninvited formation of ice crystals. For prevention of these formations, additives like glycols mono ethers, methanol, propanal are added.

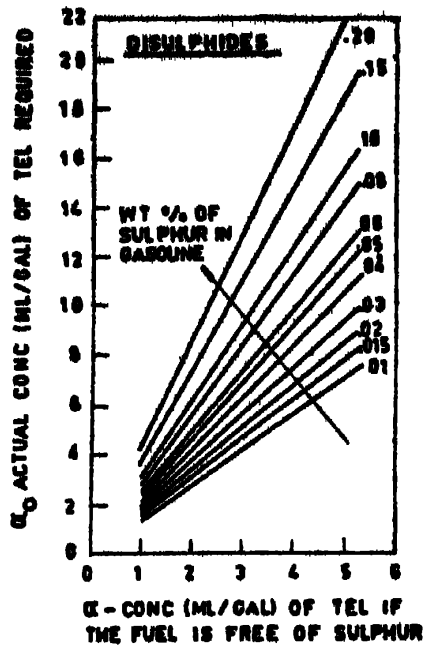


FIG. 217(a)

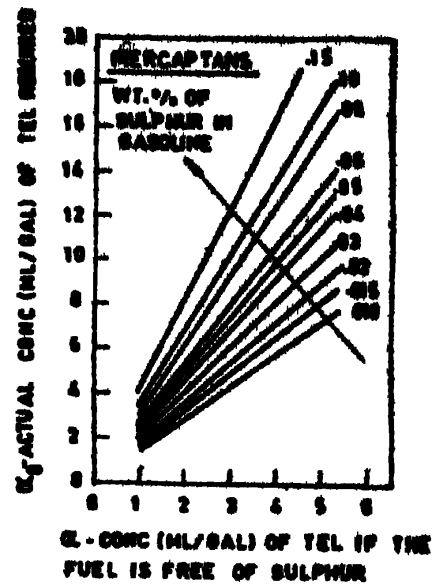


FIG. 217(b)

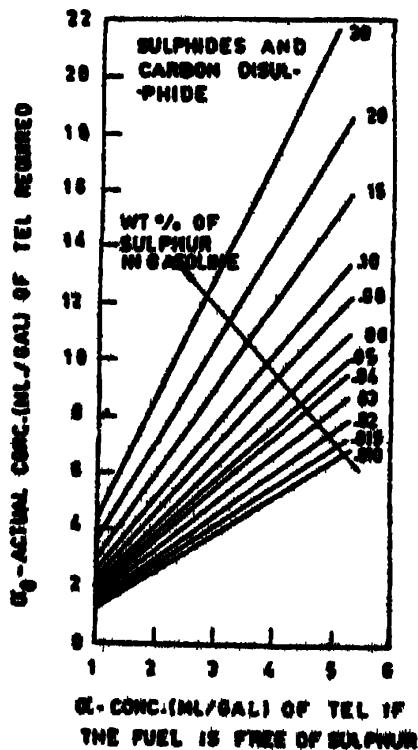


FIG. 217(c)

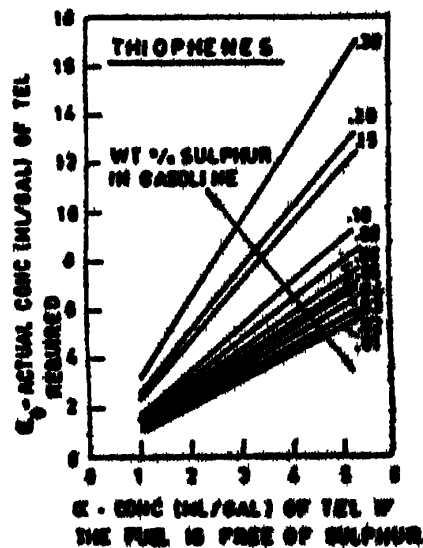


FIG. 217(d)

FIG. 217. a, b, c, d Effect of Sulfur Compounds on Lead Requirement

(a) Disulphides

(b) Mercaptans

 (c) Sulphides & CS₂

(d) Thiophenes

It is true, where moving parts are present a timely lubrication is demanded. Carburettor detergents take care of smooth function of carburettor. For free piston movements; rapid erosion of deposits in combustion chamber, lubricants and some scavengers are essential. The deposits are mainly due to decomposition of lube oils and carbon formations by frictional heat and combustion heat.

Maleic anhydride, polyamines, poly isobutylenes, phenol epichlorohydrin—amine products are some such detergents in service. As an example phenol—aldehyde amine condensate products reduce the deposits by 73% just by addition²² of 63 ppm. Petroleum sulfonates are cheaply available additives for smooth lubrication

2.3.3.2. *Inhibitors (corrosion)*

Storage and transportation of petroleum products is unavoidable. Rust prevention in these periods is essential. This is done by incorporating selective additives in products. These additives form a layer of coating on the metals and protect from rusting. Ammonium sulfonates, organo phosphoric compounds are such additives. Magnesium and silicon compounds are used for prevention of lead corrosion.

Oxidation inhibitors

Oxidation may be accelerated by metallic impurities like copper and its alloys unsaturates always have an inclination to react with atmospheric oxygen leading to gum formation. This is due to free radical mechanism. Hence the inactivation or termination of these free radicals ensures inhibition to oxidation. Anti-oxidants like phenols, cresols, phenylene diamines, alkyl amino phenols serve the purpose. Copper corrosion can be prevented by addition of disalcyledine and aminopropanes. Gasoline stabilised with *n*-oxydiphenyl amine was found to be without deterioration, even after two years²³. Without additives gasoline should not be stored for more than six months.

2.3.3.3 *Combustion Aids*

The deposits in the combustion chambers often glow and cause the fuel to burn untimely and contribute knocking. Boron com-

pounds²⁴ (organic) in small amounts not only decrease the combustion deposits but also increase the effectiveness of antiknock-ing agents.

Organo phosphorous compounds²⁵ can also reduce surface ignition by forming a refractory layer and preventing glows. Phosphates of lead, having higher glow temperatures, really impressed the manufacturers to go for high compression ratio engines.

2.3.3.4 *Anti-knocking Agents*

Tetraethyl lead is the most important of all the additives of gasoline. Though working mechanism is not convincingly reported, it is assumed to decompose into free radicals of organic nature and lead. The ions of lead try to stop the propagation of flame, thus establishing an instantaneous combustion, which favourably decreases the knocking effect, but pollution due to oxides of nitrogen increases. Further, lead compounds accumulate in engine parts. This has to be met by suitable scavengers like dibromomethane additive. With stringent pollution laws, refineries do produce unleaded gasolines of premium and regular grades. Tetramethyl lead is also employed in place of tetra ethyl lead. Modern tendency is to add a single suitable additive that can take care of all these additives. One such additive gaining importance is methyl cyclopentadienyl manganese tricarbonyl.

2.3.3.5 *Dyes*

Though dyes do not have special contributions towards gasoline properties, still they are incorporated for obvious reasons, namely to identify, to assess if there is any deterioration in gasoline during storage and to impart pleasing hues especially when cracked gasolines are blended. Pink colour is used for automobile gasoline, while light blue colour is added for aviation gasoline.

Quantities of Additives

Additive	Quantity
1. Antiknocks, TEL	0—3 ml/5 liters
2. Anti oxidants	1—8 kgs/1000 bbl
3. Metal deactivators (salicyledene)	0.5—2 kgs/1000 bbl
4. Corrosion-preventers	10—50 ppm
5. Preignition preventors/ Combustion aids	0.01—0.02%
6. Anti icing agents	1/2—1%
7. Dyes and colours	traces

The specifications of gasoline are shown in Table 2.6.

TABLE 2.6 SPECIFICATIONS : MOTOR GASOLINE, 83 RESEARCH

Sl. Characteristics No.	Method	Unit	Requirement
1. Colour	Visual	—	Orange
2. Copper strip corrosion for 3 hours @ 50°C	P : 15		Not worse than No. 1
3. Density @ 15°C	P : 16	g/ml	To be reported
4. Distillation :			
Initial Boiling Point		°C	To be reported.
Recovery upto 70°C, Min		%vol.	10
Recovery upto 125°C, Min		%vol.	50
Recovery upto 180°C, Min		%vol.	90
Final Boiling Point, Max		°C	215
Residue, Max		%vol.	2
5. Octane Number (Research Method), Min	P : 27	—	83
6. Oxidation Stability, Min	P : 28	Mints.	360
7. Residue on Evaporation, Min	P : 29	mg/100 ml	4.0
	(Air Jet Solvent Washed)		
8. Sulphur, Total, Max	P : 34	%wt	0.25
9. Lead Content (as Pb), Max	P : 37	gm/l	0.56
10. Reid Vapour Pressure @ 38°C, Max	P : 39	kg/cm ²	0.70

2.3.3.6 Aviation Gasoline

Gasoline used in aircrafts has more stringent specifications than motor spirit, although, it contains all the additives meant for motor gasoline. Sulfur content and paraffin content are more injurious to this fuel, as the operation under -60°C is severely hampered due to crystallisation of paraffin compounds. Sulfur is presumably kept below 0.05%, to eliminate the possible pollution and corrosion problems. With the advent of modern jet engines, the demand for aviation gasoline is gradually falling.

Cracked products in aviation gasolines are not permitted due to their chemical behaviour of giving inimical deposits, i-paraffins and naphthenes are preferred and form bulk of constituents. n-paraffins and aromatics follow. Aromatics (Max. 12%) are also not very much desirable (their presence is greeted very much in motor gasoline), as they do not possess high anti-knock characteristics under lean mixtures, but their performance is excellent during take off (rich mixtures). Iso octane and other alkylated products are in immense demand because they suit in close boiling ranges of aviation gasoline ($35-170^{\circ}\text{C}$) with high octane member.

All the tests needed for motor gasoline are well applied to this also. As a special case the sum of 10% and 50% ASTM distillation temperatures must not be less than 135°C . This is required to control excessive volatility. Final boiling point is kept in the vicinity of 170°C . Reid vapour pressure is less than motor gasoline and is kept around 0.4 to 0.49 kg/cm².

2.3.4 AVIATION TURBINE FUELS (ATF), JET FUELS

Modern jet engines use fuel similar to kerosene. It is a most flexible fuel in its boiling range (upto 300°C). All properties which are desirable for kerosene are considered to be sufficient. Pour point of this fuel is of extreme importance and should not be higher than -30°C as international flights always visit lands of caprice climates. High smoke point is essential for clean combustion. Smoke is contributed by aromatics and is made of high carbon to hydrogen ratio molecules called carboids which can be distinguished from coke. Naphthenes have good smoke point and illuminating characteristics, hence preferred in these fuels. To elevate the smoke

point, aromatics should be either converted to naphthenes or physically removed. It is thus required to keep aromatics in limits of tolerance upto 20%. Unsaturates estimated by Bromine number are kept below 5% to limit gum formation. Sulfur is fairly tolerated, unlike gasoline. Different aviation grades like JP—1, JP—2, JP—3, JP—4, JP—5 are used in U.S.A, while in India two grades K 43 and K 50 are produced. (See Table 2.7)

Smoke point is an important property of jet fuel. Sometimes instead of expressing the quality of jet fuel by smoke point alone, it is expressed in terms of smoke volatility index defined as

$$\text{Smoke volatility Index} = \text{Smoke point} + 0.42 \\ \times (\% \text{ distilled at } 204^{\circ}\text{C})$$

The advantages gained by this expression are still not clear. The tests prescribed for this fuel are

- (1) Volatility (ASTM)
- (2) Pour point
- (3) Smoke point (combustion quality)
- (4) Water retention and separating properties

Volatility had already been discussed ; pour point and smoke point are discussed in the kerosene and lube oil tests.

Jet fuels being denser and viscous than gasoline, they tend to retain fine particles and droplets of water for a considerable amount of time. Although filtration system can remove fine particles, it is no use for water droplets, water droplets can be removed by either heating or adding demulsifying agents. Maximum permissible limits of impurities are for fine particles 1 mg/litre and moisture content 30 ppm. Free water in jet fuels can be detected by field kits like Esso-hydro kit, Mobil Moisture Indicator. The standard water reaction test (IP 289) is used as in the case of aviation gasoline. The clarity of fuel is measured by photo electric device.

Noticeable phenomenon during high altitude flights and at high speeds is that fuel gets charged. To disperse these static charges antistats are added.

TABLE 2.7

<i>Aviation Turbine Fuel</i>		
	Grade K43	Grade K50
Acidity in grains	Nil	Nil
Aromatic % vol. max.	20	20
Bromine number, max.	5	5
Colour Saybolt, min.	8	8
Copper strip corrosion 2 hrs. at 100°C. Not less than No. 1		
Distillation		
(a) I.B.P.	Not limited but to be reported	
(b) Recovery upto 20% by Volume	-do-	
(c) Recovery upto 20%	200°C minimum	
(d) Recovery upto 50% by vol.	Not limited but to be reported	
(e) F.B.P. max.	300°C	300°C
(f) Residue, % age vol. max.	2	2
(g) loss percent by vol. max.	1.5	1.5
Flash point min.	38°C	38°C
Cold test temp. max.	-40°C	-50°C
Residue on evap. max. mg/ 100 ml	3	3
Gum accelerated (16 hrs.) mg/100 ml. max.	6	6
Cal. value Cal/gm. (min.)	10167	1016
Density at 15°C	0.775 to 0.825	0.77! to 0.82!
Sulfur by vol.	0.005	0.00!
Sulfur, total, percent by wt.	0.02	0.2
K.V. at -17.8°C (CS)	6	6
Water reaction Change in vol. of ether layer max.	1 ml	1 m'

The paraffin rich fuels can allow micro organisms to survive, for this reason, when these fuels are allowed to be stored over great period, biocides are added. Other additives are also used as in the case of aviation gasolines. Additives and their functions are presented below :

<i>Additives</i>	<i>(Purpose) Quantity</i>
Poly sulphones	Antistats 1 PPM
Organic boron compounds	Biocides (20 PPM element boron)
Phosphoric compounds	Rapid combustion aids in ram jets (200 PPM)
Glycol, polyhydric alcohols	Anti icing agents upto 1%

For jet fuels adequate information has not been provided by smoke point alone; a better method is by prescribing luminometer number (ASTM D-1740). Satisfactory luminometer numbers for some grades are given as

$$\begin{aligned}\text{For JP}_1 &= 51 \\ \text{JP}_4 &= 60 \\ \text{JP}_7 &= 75\end{aligned}$$

Further, the smoke point of fuel can indicate the percentage hydrogen content of fuel²⁷ as shown by the relation

$$\text{H}_2\% = 12.99 + 0.04 \times (\text{smoke point in mm})$$

2.3.5 NAPHTHAS

These fractions are highly volatile and fall in the boiling range of motor spirits. These are mostly used as solvents in paints, perfumery and other industries. Solvent grades are produced by distilling wide cut naphthas into small boiling range cuts. Naphthas are not suitable for combustion, because of the rapid flame propagation, resulting in explosions. Cuts boiling below 80°C do not have any aromatics, hence their solvent power is also less. Such fractions are sent for cracking operation. 80-120°C fraction is reformed to improve octane number and this goes as a blend into straight run gasolines.

General requirements of solvent naphthas are

1. Almost water white in color
2. Non-corrosive nature

3. High stability
4. High solvent power (Kauri Butanol test ASTM D1133)
5. Low boiling point
6. Low acidity

Suspended impurities are removed by filtration. Solvent power is determined by Kauri Butanol number. The volume of solvent that cause a standard Kauri Butanol gum in butyl alcohol to become a 10 point type illegible when viewed through this solution. Another method of estimation of solvent power is by Aniline point. Harvey^{29a} Mills relationship for KBN is given by

$$\text{KBN} = 99.6 - 0.806 G - 0.09912 A + 0.0755 (340 - B \times 0.56)$$

(For less than 50)

where $G = \text{Sp. Gravity}$

$A = \text{Aniline point, } ^\circ\text{C}$

$B = \text{Mid boiling temperature } ^\circ\text{C}$

2.3 6 KEROSENES

Kerosene is the general name applied to the group of refined petroleum fractions employed as fuel and illuminant. All these fractions have approximate boiling range 150—250°C. These are uniform close cut distillates, low in viscosity, with a good degree of refinement to be fairly stable, light in colour and free from smoky ill smelling substances. It is highly desirable that sulfur be kept as low as possible. Kerosene is used as illuminating oil in domestic needs both in wick burners and mantle burners. Though obsolete these days, it was used in railway signalling purposes. Such kerosenes were special blends of relatively high boiling fractions with oils of marine animals.

Tests and properties of kerosene :

1. Flash point and Fire point
2. Smoke point (Burning quality)
3. Volatility
4. Sulfur content
5. Aniline point

Above listed properties are cardinally judged for kerosenes of all grades. Specifications for superior kerosene are given in Table 2.8.

TABLE 2.8
SPECIFICATIONS KEROSENE (SUPERIOR)

Sl. No.	Characteristics	Method	Unit	Requirements
1.	Acidity, Inorganic	P : 2	mg KOH/gm	nil
2.	<i>Burning Quality</i> : Char Value, Max Bloom on Glass Chimney	P : 5	mg/Kg of oil consumed	20 Not darker than grey 21
3.	Colour (Saybolt), Min	P : 14		21
4.	Copper Strip Corrosion for 3 hours. @ 50°C	P : 15		Not worse than No. 1
5.	<i>Distillation</i> : Recovered @ 200°C, Min Final Boiling Point, Max		% vol. °C	20 300
6.	Flash Point (Abel), Min	P : 20	°C	35
7.	Smoke Point, Min	P : 31	mm	20*
8.	Sulphur, Total, Max	P : 34	% wt	0.25**

* For supplies to Defence, the smoke point of product shall be 21 mm minimum

** For supplies to Defence, the total sulphur, per cent weight, shall be 0.20 maximum.

2.3.6.1 *Flash point*

This is defined as the minimum temperature at which the vapours from oil sample will give a momentary flash on application of a standard flame under specific test conditions. Abel (P : 21 ; IP 170/59) Pensky-Martens (P : 21 ; IP 34/58) Cleveland are the test apparatus frequently used for the purpose. Significance of the flash point is that it can predict the possible fire hazards during transportation, storage and handling. Early tendencies were to incorporate more volatiles in kerosenes, thus inviting unusual fire hazards. This necessitated a strict vigilance by way of fixing flash point. The flash point of marketable kerosene should be above 42°C.

Pensky-Martens Apparatus (P : 21 ; IP 34/58) and Test :

The apparatus consists of a cylindrical cup made of brass of approximate dimensions $50.8 \pm 1.27 \text{ mm} \times 55.88 \pm 1.27 \text{ mm}$ (height inside) with a thickness at the bottom $2.41 \pm 0.64 \text{ mm}$. Inside the cup at $2/3$ rds height from the bottom there is a sudden and slight tapering up to the top of the cup. This looks like a ring and guides as a filling level for the sample. The top position acts as a vapour-air chamber.

This cup is provided with a lid, and the lid is actually made of two metal discs, one sliding over the other. The lid also includes (a) stirring device (b) two flame-holders, one test flame and other pilot flame (c) provision for thermometer (d) spring handle. By turning the spring handle, it is possible to slide one lid over the other whereby the exactly cut chords align with each other, exposing air-vapour mix of the cup to flame. In fact, there are three chord openings, central one is meant for flame introduction, while the other two act as air introducers. When the handle is turned test flame is also simultaneously lowered into the central chord opening to explode air-vapour mixture. The test flame is issued from an opening of 0.69 mm dia. The whole cup is heated by air-bath, which is primarily heated by electric power.

The test sample is filled up to the mark, and the temperature of the oil is slowly and uniformly raised at a rate of 3°C per minute. Test and pilot flames are lighted. Occasional stirring is done. The spring handle is rotated at every 1°C raise in thermometer; till a bluish light flash is noticed. Heating should be maintained at the prescribed rate.

Abel flash meter is used for highly volatile samples, whose flash point shall be less than 40°C . Pensky-Martens closed cup can be used for medium flash liquids, when a high flash point liquid is to be tested open cup flash meter is convenient.

Flash point is essentially dependent up on the light end characteristics of a fuel. Approximate relationship between flash point and IBP -10% boiling range is given by Nelson²⁰⁰ as

$$\text{Flash point} = 10.92 (T^\circ\text{C}) - 79.52$$

Flash point is regarded as vapour property hence the ambient pressure directly influences the flash point. Thus one is reminded to note the ambient pressure before such a test is conducted. Cor-

rection for pressure may be accorded by applying the following relation :

$$\text{Flash point } T^{\circ}\text{C} = \text{Flash point } (t^{\circ}\text{C}) \text{ at } 760 \text{ mm. Hg} + \frac{760 - P}{30}$$

where P is the pressure in millimeters at the time of observation. Flash point of blends does not follow any linearity : however the influence of high volatiles (range of 0—10% distillation) is predominant. Instead of laborious theoretical correlations it is always easy to determine the flash point of mixtures experimentally as shown in Fig. 2.18.

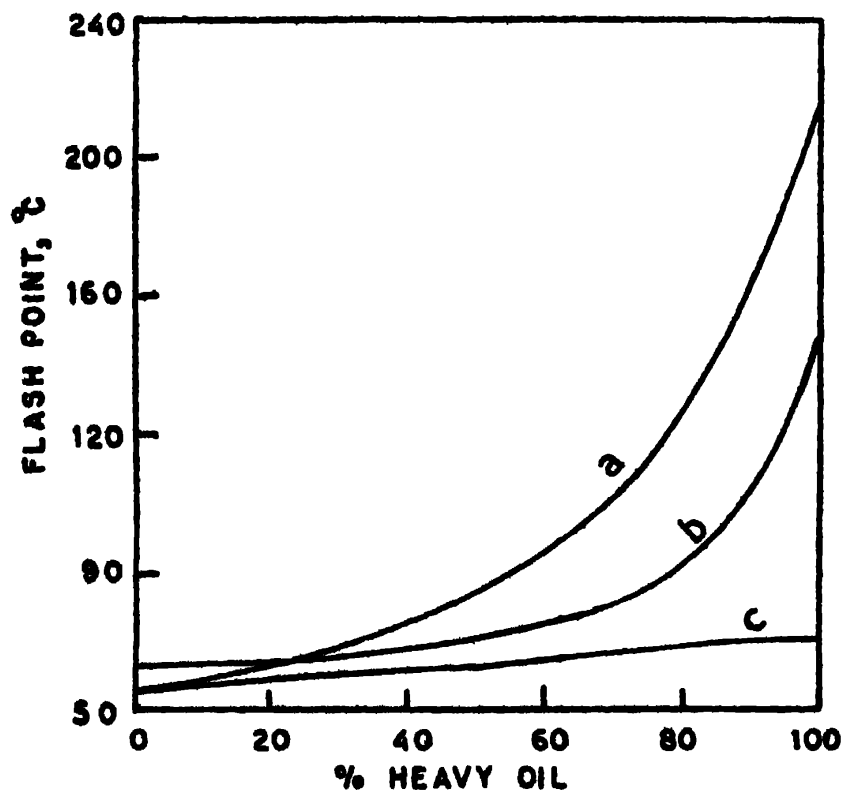


FIG. 2.18. Flash Point of Blends. a, b, c Curves show different blends of heavy and light oil

2.3.6.2 Fire point

This closely follows the flash point. The test is carried out in open cup rather than a closed one. Cleveland apparatus (ASTM D 92) offers the advantage of open flash point and fire point. Fire point temperature is noted when the oil vapours can burn continuously for 5 seconds when tested in flash point apparatus and it occurs after the flash point, by 3-4°C. For domestic

needs a very high flash point above 50°C is also not desirable. The easy ignition is credited to volatiles only and decrease in volatiles enhances the flash point causing difficulty in ignition.

2.3.6.3 *Smoke point*

Smoke point is an indication of clean burning quality of kerosene. Illumination depends upon the flame dimension although it is not related to flame height. Many paraffins may be gifted with better flame heights but illumination may be poor. Smoke point is defined as the maximum height of flame in millimeters at which the given oil will burn without giving smoke. Thus smoke point test (P : 31, IP 57) enables the burning quality to be measured by adjusting the wick height to give proper non-smokey flame (Fig. 2.19). Illumination is supposed to be characteristic of the components of fuel usually not measured. Different flame heights are obtained due to the presence of different components such as paraffins, naphthenes and aromatics.

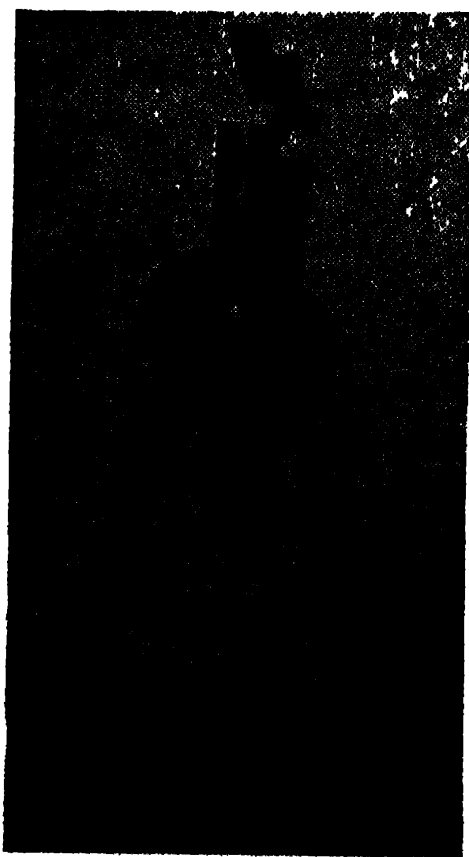


FIG. 2.19. Smoke point apparatus

Aromatics contribute smoke, hence removal of aromatics increases the smoke point. Naphthenes with side chains one inevitably retained to give good illumination. In Ind'a, marketable kerosene should possess a smoke point 18 mm. Smoke point may be predicted approximately by knowing the group composition of oil. given as :

$$\text{Smoke point} = 0.48 P + 0.32 N + 0.20 A.$$

where P, N, A are % of paraffins, naphthenes and aromatics in the sample.

A dogma of high smoke point meant a better quality fuel is not always acceptable as it can not specify any illumination characteristics. In recent literature stress is given to this luminosity number (ASTM D 1740) and prescribed as a test for kerosene. This indicates luminosity of the flame and accompanying radiation problems in combustion chambers. Smoke point apparatus with modifications to include a photo electric cell can measure the flame radiations. Luminosity number is expressed just like octane number. The constituents taken here are tetralin (0 luminosity number) and iso octane (100 luminosity number). The blend of these two should match with the luminosity of fuel.

2.3.6.4 *Burning Quality Test* (P : 5 ; ASTM D182)

This indicates the ability of kerosene to burn steadily and cleanly over a long period. Kerosene is tested by burning in a standard wick lamp for a period of 24 hours, in a room free from air currents. The average rate of burning, change in shape of flame, the density of chimney deposits are the prime factors by which the quality of kerosene is assessed. A good quality kerosene (after burning for 16 hours) should present the chimney as clean as possible (only slightly clouded) and the wick should not have any appreciable hard incrustations with as large flames as in the beginning.³⁰

The continuity of the initial illumination over long periods in a lamp rests on the normal flow of kerosene to the wick end. Quantity of oil available at the tip of wick depends on the height

of wick over liquid surface, texture of wick and properties like viscosity and surface tension of oil. Even though surface tension of different oils (kerosenes) may not vary much, viscosity varies. Stabilisation of flame is governed by viscosity. A good oil of 650 c.c must burn at least for 120 hours.

2.3.6.5 *Volatility*

The nature of distillation range estimated by ASTM D 86 is of significance with regard to burning characteristics. Ten percent boiling point reveals the flash point which in turn, indicates the ease of ignition ; specially when kerosene is used in pump stoves, this plays a very important role in continuous support of flame. Mid boiling range contributes towards viscosity. Often flare up in oil heaters is observed if mid-boiling range is not properly constituted. Sixty percent distillation at 200°C ensures steady performance of oil in heaters. Minimum of 15% distillation at this temperature is enforced to guarantee adequate volatility^{41a}.

2.3.6.6 *Sulfur content*

High sulfur content is inimical due to its combustion products. When large amounts of such fuel is burnt, accumulation of these oxides results, offering wayward problems of corrosion and pollution. Total sulfur can be estimated by bomb method (ASTM D 1266 ; IP 107). Maximum permissible amount of sulfur is 0.13% ; in all kerosenes.

2.3.6.7 *Aniline Point*

(IP 2/56 ; IS (1448) P : 3) This test indicates qualitatively the amount of aromatics present in kerosene. This method is fully discussed in diesel fuels.

2.3.7 DIESEL FUELS

Diesel oils are the fractions in the boiling range of 250-320°C ; and fall under gas oil fractions. These are basically divided into two classes as high speed diesels and low speed diesels.

Classification of diesel oils is done according to speed and loads of the engine as given below :

Low speed	Below 300 RPM	For heavy loads at constant speeds.
Medium speed	300-1000 RPM	Fairly heavy loads moderately constant speeds.
High speed	above 1000 RPM	Load and speed vary.

Volatility test for these fuels is of trifle value ; however it is advisable to conduct ASTM distillation test to infer the boiling range. High percentage of light ends (upto 10% distillation) are traits of low flash points. Even though flash point has no direct influence upon performance of fuel, still its minimum value should be maintained to prevent possible fire hazards in handling and storage. If 10%—50% boiling temperature is high, its warm up period will considerably increase. A high boiling point gives much smoke formation and crank case dilution. For all high speed oils 50% point is kept around 300°C ; too low 50% point gives a low viscosity and possibly low heating value too. Table 2.9 gives specifications of high speed diesels.

The general tests recommended for diesel fuels are (in the order of performance).

- (1) Pour point
- (2) Aniline point—Diesel Index (Cetane number)
- (3) Flash point
- (4) Calorific value
- (5) Viscosity

2.3.7.1 *Pour Point*

The criteria of pour point fixation depends upon two factors namely climatic conditions and storage (handling). Fuel, at minimum ambient temperature must be free flowing. In India pour point is fixed at 5°C ; however in the Himalayan belt, where the climate persists at sub-zero level this may not be satisfactory ; hence low pour point oils are essential. It is also observed that at close approach of pour point (within 2 to 3°C), the viscosity increases very much, the result of which is high pumping costs.

TABLE 2.9

SPECIFICATIONS : HIGH SPEED DIESEL OIL

Sl No.	Characteristic	Method	Unit	Requirement
1	Acidity, Inorganic	P : 2	mg KOH/mg	Nil
2	Acidity, Total, Max	P : 2	mg KOH/mg	0.50
3	Ash, Max	P : 4	% wt	0.01
4	Carbon Residue (Ramsbottom), Max	P : 8	% wt	0.20
5	Pour Point, Max	P : 10	°C	6
6	Copper Strip Corrosion for 3 hrs @ 100°C	P : 15		Not worse than No. 1
7	Density @ 15°C	P : 16	g/ml	To be re-reported 45 min
8	Diesel Index	P : 17		
9	Distillation : Final Boiling Point	P : 18	°C	To be re-reported 85/90
	Recovery @ 366°C, Min			33/38*
10	Flash Point, (Abel), Min	P : 20	°C	2.5—7.5
11	Kinematic Viscosity @ 37.8°C	P : 25	cS	
12	Sediment by Extraction, Max	P : 30	% wt	0.05
13	Sulphur, Total, Max	P : 33	% wt	1.1 **/1.0
14	Water Content, Max	P : 40	% vol.	0.05
15	Flame Height, Max	Indian Customs	mm	18

* Subject to agreement between the purchaser and supplier, a lower or higher maximum Flash Point may be accepted.

** Subject to agreement between the purchaser and supplier a lower or higher maximum Sulphur Content may be accepted.

2.3.7.2 Aniline Point

Diesel fuels are mainly composed of paraffins although there is no bar for aromatics. Aromatics of this boiling range present in the fuel cause abnormal ignition delay. For this reason an estimation of aromatics is essential. One such method is aniline point which can predict the suitability of oil. Aniline point is defined as the minimum temperature at which equal volumes

of anhydrous aniline and oil mix together. Diesel index (IP 21/53 ; IS P : 17) a derivative of Aniline point is defined as

$$[0.018 \text{ A.P } ^\circ\text{C} + 0.32] \text{ API.}$$

Aniline being an aromatic compound freely mixes with aromatics ; so a low aniline point indicates, low diesel index (because of high percentage of aromatics). Aniline point can also predict the amount of carbon present in the molecule (aromatics), as given by the formula³⁷.

$$\% C_A = 1039.4 n_D^{20} - 470.4 d_{20} - 0.567 \text{ AP}(^\circ\text{C}) - 1104.42$$

where n_D^{20} . refractive index at 20°C

d_{20} density at 20°C

Diesel index is a measure of ignition quality of fuel. Diesel engine works on the principle of compression ignition. During compression adiabatically the air temperature reaches around 600°C , when the fuel in finely atomised form is fed in, it instantaneously explodes. The temperature at which this explosion takes place without the aid of fire is called self ignition temperature. Self ignition temperature is low for paraffins while it is high for aromatics (benzene 651°C) (See Chapter 2.2). Thus a fuel rich in aromatics burns later causing ignition delay and it gives rise to what is known as diesel knock. For this reason all diesel fuels are processed to have a diesel index in the range of 45 to 55. A high diesel index is also not desirable, as a fuel rich in aromatics gives rise to better calorific value than paraffin rich fuel for equal weights. When the fuel is injected into the chamber of hot air, first the fuel drops acquire the temperature of the surroundings. This takes some time. The time delay can be decreased by atomising the fuel into fine drops and also by varying the composition of fuel. Viscosity also has its own role in heat transmission. Once the droplets acquire the temperature of self ignition, the droplets explode. A continuous flame front may move if the aromatic rich fuel is fed in—obviously a cause for diesel knocking. Fig. 2.20 shows the diesel fuel performance in an engine. During adiabatic compression, the temperature rises and at that instant the fuel is injected. The time taken by the fuel, from injection to explosion is known as delay period. Then the fuel burns at a constant rate. The air pressure and temperature increase after explosion. The two curves A & B

marked in the figure show the characteristic performance of two fuels—'B' is for a fuel rich in paraffins and 'A' is for aromatic rich fuel.

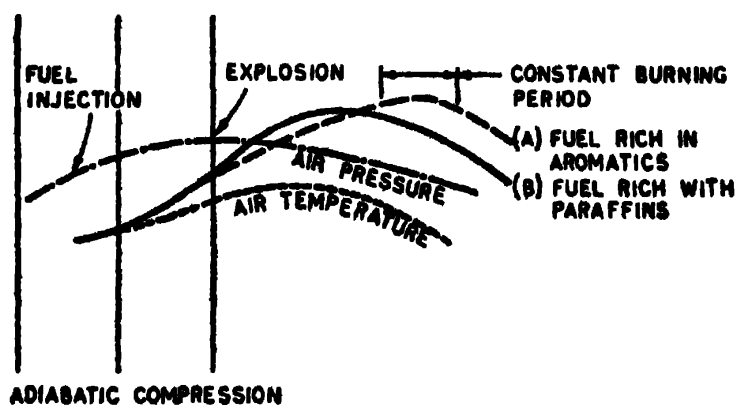


FIG. 220. Diesel oil Combustion Performance in Engine

Peaks *a* and *b* obviously should coincide with crank position, otherwise, knocking results. High speed engines require a fuel of viscosity, 1.4 to 2.5 CS (at 30°C), where as low speed engines may work with even high viscous fuels (5.8–26.4 CS).

Cetane number : (IS P 19 ; ASTM D 613-58T)

Cetane number is a corollary of Diesel index.

It is defined as percentage volume of *n*-cetane in a mixture of *n*-cetane and α -methyl naphthalene, which gives the same ignition delay as the fuel under consideration, when tested in a CFR engine. Some people prefer heptamethyl nonane (Cetane No. 15) in place of α -methyl naphthalene.

A relation between diesel index and cetane number is presented in Table 2.10(a).

TABLE 2.10(a) : Cetane number Vs. Diesel Index.

<i>Cetane No.</i>	<i>Diesel index</i>
30	26
35	34
40	42
45	49
50	56
55	64
60	72

TABLE 2.10(b) : Diesel Fuel Ease of Starting

Ambient Temperature °C	Cetane No.	Viscosity SSU at 37.8°C
-34.4	90	—
-28.9	83	46
-23.3	76	57
-12.2	63	65
- 6.7	56	—
- 1.1	49	—
+ 4.4	43	100
+10.0	36	—

TABLE 2.10(c) : Diesel Fuels—Properties

	<i>High speed</i>	<i>Low speed</i>	<i>Medium speed</i>
Viscosity at 37.8°C			
SSU Minimum	32		32
Maximum	50	250	70
Sulfur %	1.5	2.0	1.5
Conradson Carbon Residue %	0.2	3.0	0.5
Ash %	0.02	0.04	0.02
Water and Sediment % vol.	0.05	0.6	0.1
Flash point °C	—	62.3	62.3
Cetane No.	50	30	40
Diesel Index	45	20	30

2.3.7.3 Flash Point

It has no real significance on performance of fuel. Knowledge of this is required for safe handling and storing. In India flash point of diesel is kept around 50°C—55°C.

2.3.7.4 Calorific Value

Though high calorific value of the oil is desirable, it cannot be at the expense of diesel quality; hence a fuel having^{29b} calorific value 41.83 kJ per gm is sufficient. Apparently paraffins have high calorific value due to higher hydrogen content, but aromatic

tics mainly contribute by bond dissociations. The disparity in calorific value for these materials in this region is not overwhelming.

2.3.7.5 *Viscosity*

Ease of starting depends upon viscosity and ignition quality. At lower starting temperatures high cetane fuels are required (See Table 2.10(b)). Diesels used for different speeds must possess the properties as shown in Table 2.10(c).

Thermal stability of diesel fuels is important, because the remaining fuel from the combustion chamber is returned back to the reservoir. The test is performed by exposing 50 ml sample kept at 149°C for 90 minutes with an additive. When the sample is filtered through a filter paper, the excessive stain on filter paper is an indication of bad oxidation stability of the fuel usually additives like 1-n-butoxy-1-ethane, dioctyl-diphenyl amine (upto 20 ppm, are used to improve the stability of fuel.

2.3.7.6 *Diesel Additives*^{88, 89}

Just like gasoline, diesel fuels are also blended with additives to give satisfactory performance. Ignition accelerators are used for reducing the ignition delay. These are generally oxygen donating substances (oxidising type) like nitrates and nitrites of C₇-C₈ acids (amyl nitrate is an example); aldehydes, ketones, ethers and peroxides. These have the tendency to oxidise the fuel. Inhibitors to stop gum formation are the same type as used in the case of gasoline (phenol amines under the trade name Topanol).

Pour point depressors are generally chlorinated paraffins, and these are used to improve the cold-start performance of the engine. Anti-smoke additives like ethyl lubrizols cause less smoke in the exhausts. Alkaline agents and ashless dispersant additives have been used to improve quality of rail diesels. These alkaline agents provide improved piston ring and cylinder line protection particularly with high sulfur fuels.

Antistatic additives are optional because of the ubiquitous demands of diesel; time of storing is not much, hence these may or may not be mixed. Usually these are the chromic salts of alkylated salicylic acid, calcium aerosols, vinyl methacrylate

polymers. To prevent microbiological growth dioxaborinanes (boron compounds) N-benzylidenemethyl amine are used.

2.3.8 LUBE OILS

The principal source of lubricating oil is the fraction that is left after lighter components, namely gasoline, kerosene, diesel oil during crude distillation. Generally lubes have a boiling point above 350°C and these are obtained as the main products from vacuum distillation units. Residuums, after precipitation of asphaltenes are known as bright stocks and form a good source for lube oils.

2.3.8.1 *Composition of lube oils*

Lubricating oils are composed of paraffins, naphthenes, aromatics and unsaturated bodies. The chief molecular structure of lubes seems to be naphthene rings or naphthenes and aromatic rings arranged in groups of as many as six with paraffinic side chains. The more such chains the more paraffinic the oil is. Naphthenic crudes give more rings with less side chains. Normal paraffins (long chains) in this range are usually waxy in nature and have to be separated for maintaining free flow of oil. Thus a crude oil rich with paraffinic chains gives high viscosity index, less viscosity gravity constant and high stability lube oils. Depending upon the services intended for, lube oils are classified. Nelson²⁹⁰ grouped the oils into seven categories as shown below :

- (1) Machine and Engine Oils (Neutral oils)
- (2) Compounded Oils
- (3) Turbine Oils
- (4) Cold test Oils
- (5) Transformer Oils
- (6) Colour Oils (White Oils)
- (7) Corrosive Oils

2.3.8.2 *Machine oils & engine oils*

These are all high viscosity index oils as they have to serve under varying temperatures. Medium viscosity oils are suitable for most of the industrial applications. Low viscosity index oils

are suitable for compression ignition engines, Aircraft engines require a very high viscosity index oils. These oils are further subdivided into straight, premium, heavy duty, etc. depending upon viscosity index and serviceable temperature. These oils also include spindle oils of (HVI). These are produced from HVI, neutral or bright stocks. Cylinder oils are also HVI grade oils, but at⁴⁰ present our country does not produce them. The availability of bright stock and HVI neutral is at present satisfactory.

Marine grade oils are required to meet critical necessities of performance. Thus, these stocks are produced in our country as blends from indigenous and imported oils. Aviation oils are also special grade oils ; such oils are not produced in India at present. The oils which are used in different services are shown below :

HVI oils for planes, high speed operations

MVI oils for petrol, diesel and stationery vehicles

LVI oils for light equipment.

In fact no single oil is suitable for all types of applications. This has called for blends of multigrade oils. All multigrade oils contain viscosity improvers. As an example, a multi grade blend of SAE 30 and 10W, can have the starting viscosity corresponding to that of SAE.10W, while in operation it can show the characteristics of SAE 30. The trend of viscosity variation of such blend is shown in Fig. 2.21.

2.3.8.3 *Compounded oils*

These are lube oils fixed with animal or vegetable oils. These oils exhibit more wettability characteristics which makes them suitable for steam engines, compressors and quenching and tempering operations. Emulsibility is considered to be more important than viscosity index of these oils.

2.3.8.4 *Turbine oils*

High speed machinery, such as steam turbines, electric motors should have emulsion-free oils. Extreme stability is required for such oils.

2.3.8.5 Cold test oils

These oils are mainly used in refrigeration and hydraulic systems, specially designed for arctic climates. Pour point is the major important thing compared to all other properties of oil.

2.3.8.6 Colour oils

These are industrial oils used in textiles, food and paper industries. Medicinal oils must be very thoroughly freed from colours and must have high stability. Depending upon the application, the concentrations of sulfur, aromatics and resin bodies are fixed.

2.3.8.7 Corrosive oils

Some oils are blended with corrosive ingredients. These are used in cutting, shaping of metals. Heavy duty oils and extreme pressure lubes are of this category.

Above classification by service is no doubt suitable for almost all applications. Physical properties are to be included for a technical classification. Accordingly SAE classification and Bureau of Ships classification have come into service, which set forth the physical parameters for application.

SAE Classification for Crank case oils¹²

(Viscosity in c.s.)

S A E No.	Viscosity range				
	at -18°C		at $+99^{\circ}\text{C}$		
	Min	Max	Min	Max	
5 W		1,300			
10 W	1,300	2,600			
20 W	2,600	10,500			
20	—	—	5.7	< 9.6	
30	—	—	9.6	< 12.9	
40	—	—	12.9	< 16.8	
50	—	—	16.8	< 22.7	

As lube oils are made for a wide variety of applications it is not possible to make a single product to meet all the require-

ments. As a consequence lubes are formulated for a particular application, hence large formulations are indubitable.

Whatever may be the special formulation, all lubes are to be submitted to tests, as given below : (Special tests are not mentioned here) :

- | | |
|-----------------|-----------------------------------|
| (a) Flash point | (c) Viscosity and Viscosity index |
| (b) Pour point | (d) Oxidation stability |
| | (e) Carbon residue |

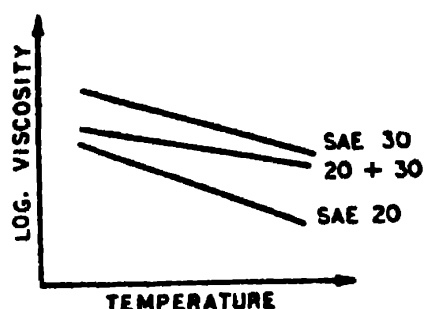


FIG. 221. Viscosity Variation of multigrade oils with Temperature

2.3.8.8 Carbon Residue

The propensity of cracking is indicated by carbon residue of the oil. Heavy oils being delicate to high temperatures, have a tendency to crack, with deposition of carbon. Lube oils are often subjected to such hazardous temperatures. The amount of carbon formed during cracking does ultimately provide an idea of usability of oil at high temperatures. This test is conducted by two methods namely Conradson method (IP13/66) and Ramsbottom method (IP 14/65 ; IS : 1448 P : 8).

2.3.8.9 Conradson method

A sample of 10 gms is taken into a silica-crucible and heated out of contact with air. The set-up provides the necessary precautions, such that the oil is thermally decomposed out of contact with air. The decomposition is brought by means of high heating rates. As the heating continues fumes appear at the chimney top. The fumes are burned and heating rate is adjusted

such that the burning sustains, but the flame is never allowed to cross the bridge of the chimney. (See Fig. 2.22). After the

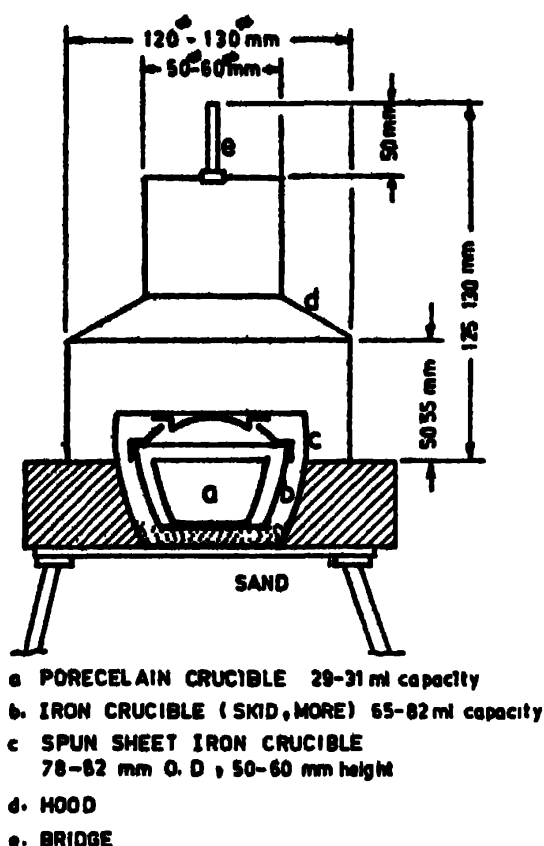


FIG. 2.22. Conradson Carbon Residue Apparatus

burning of the fumes further heating is continued. Afterwards, the set is cooled and the silica crucible is weighed to get the weight of carbon deposited. Expressed in percentage gives Conradson carbon residue.

Prescribed heating rates :

Initial heating (Fumes appear and capable to burn continuously, when ignited)

Pre-ignition period 10 ± 1.5 min.

Burning of fumes (Burning of fumes without crossing the bridge of chimney.

13 ± 1 min

Strong heating (For complete decomposition of oil)

7 min

Total time 30 ± 2 min.

If the above schedule is unable to be followed, the burning period of fumes should only be taken into account. Very high rates of heating are required to keep up the schedule.

2.3.8.10 *Ramsbottom method (Fig. 2.23)*

In this method the sample is carefully fed into a glass bulb which has a capillary end. The bulb is kept into a heating bath kept at 550°C. The sample is allowed to decompose for 20 minutes. After heating is over the bulb is cooled and weighed to find the carbon formed. Amount of material to be taken is inversely proportional to coking tendency of the oil.

Expected Carbon residue	Size of sample for experimentation
2%	4.0 gms
2—4%	2.0 gms
4%	1.0 gms

Best quality of oils give less carbon residue under serviceable conditions. Conradson carbon residue of this should not exceed 0.2 to 1.0%. Paraffin oils give less carbon residue compared to naphthenic oils.

2.3.8.11 *Oxidation stability*

This test reveals the deterioration characteristics of oil on oxidation. Oils are generally in contact with air and hot surfaces, thus oxidation is inescapable. Higher paraffins are easily oxidised compared to naphthenes and aromatics. Major amount of lube oil is paraffin, which is more prone to oxidation. In the laboratory the test is conducted (IP—48/62) by passing air at a rate of 15 litres per hour through a sample of 40 ml kept at 200°C for 6 hrs. Second oxidation period for another 6 hrs. at the identical conditions for the same sample is carried out. After oxidation periods are over, the sample is cooled and its viscosity and carbon residue are found out and compared with the original sample. Papers on the chemistry of oxidation of fuels and its inhibition have been authored by Bettoney et al⁴⁴ and Lod Wick.⁴⁵

All oils of high boiling points are susceptible to this natural oxidation which proceeds by free radical mechanism. So, inhibitors prevent the free radical chain propagation and increases

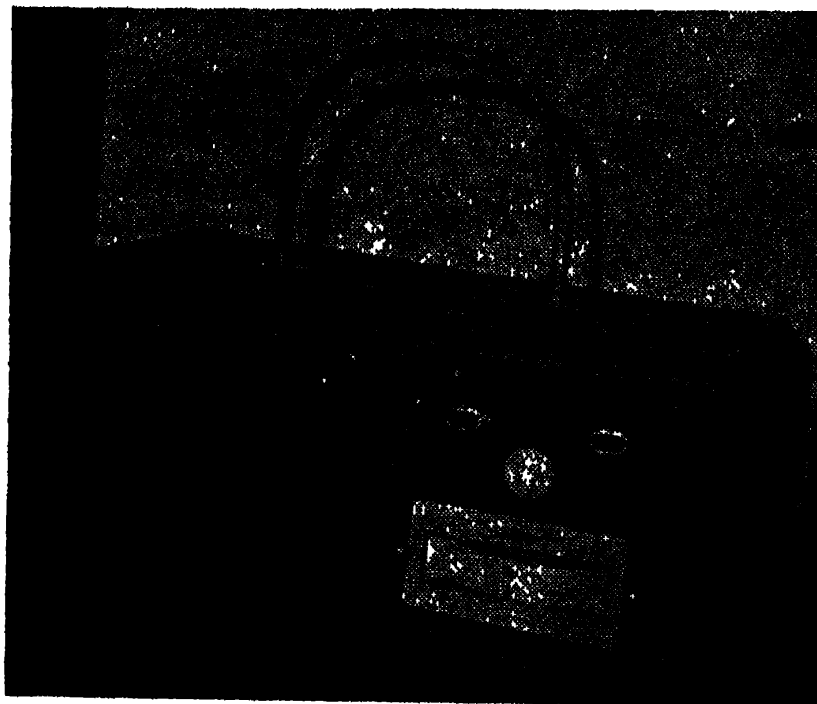


FIG. 2.23 Ramsbottom apparatus

the resistance of oil to oxidation. All oils in general are blended with such additives.

Additives and their functions in lube oils are presented in Table 2.11. Additives supplied by different companies also accompany in Table 2.12.

2.3.9 TRANSFORMER OILS

These oils are used in electrical industry mainly for insulating, cooling purposes; additionally these oils protect the equipment from moisture compared to vegetable or coal distillate oils, petroleum oils are found to be more suitable because of high viscosity, thermal stability & hydrophobic nature. Petroleum oils used in electrical industry fall into two categories^{41a}; Oils in transformers & circuit breakers etc. belong to one class; other class of oils are generally used for impregnating cables & papers used in electrical industry. Oils used in transformers are low

viscous, thermally stable but having high boiling points, in close ranges. Second type oils are highly viscous and act as insulators only. The deterioration of these oils in service is closely connected with the oxidation characteristics of oils. Oxidation products are mainly acids which cause sludge formations.

Importants tests for transformer oils

- (1) Acid value (ASTM D 974)
- (2) Dielectric strength
- (3) Flash point
- (4) Pour point
- (5) Sludge value
- (6) Copper corrosion test

2.3.9.1 *Dielectric Strength*

High dielectric strength is required for oils employed for insulation purpose. Even though high electric strength does not give any indication of degree of refinement of oil or oil contaminants, it ensures the freedom of oil from water and other adventitious matter. Electric strength or break down test is performed by increasing the voltage at a rate of 2 KV/sec in between electrodes of 12.5 to 13.0 mm dia. which are placed at a distance of 2.5 ± 0.1 mm. The cell capacity is usually between 300 to 500 ml. The voltage is continuously raised until break down takes place. A satisfactory oil test (IP 20/73) should show a break down strength of around 120 KV/cm.

2.3.9.2 *Permittivity* (dielectric constant)

It is the ratio of capacity of a capacitor in which oil is dielectric ; to the capacity of air when this acts as dielectric. The range of permittivity should lie between 2.1 to 2.3.

2.3.9.3 *Sludge Value*

Oils contain some products which give rise to sludge formation. Sludge value is found out by precipitating insolubles with heptane. This test is performed before oxidation of the oil and after oxidation of the oil. High sludge formations indicate the negative quality of oil, which also indicates the high percentage of oxidative products.

TABLE—211
ADDITIVES FOR LUBE OILS

<i>Purpose</i>	<i>Additive</i>	<i>Quantity</i>	<i>Ref :</i>
Pour point depressors (depress the pour point of lubes and other fractions for crude Laudding)	Poly alkyl metha ^a crylates ^b Maleic-fumaric esters Curene ^c	(0—1%) gives 5°C depression (0.1%) gives 10°C 0.2—0.5% for 9°C	a. J. K. Rostogi, 2 LAWASP IIT. Bombay b & c ; M. C. Dwivedi & R. Vipradas, 2 LAWASP d. N. K. Purohit 1st LAWASP, Nov. 22-23 ; 1978 IIT. Bombay. e. C. C. Colyer, 7 WPC, 1967, Vol. IV, P 294 f. H. M. Noel Pet. Ref. Manual Reinhold, P 147
Oxidation inhibitors (prevents oxidation of unsaturates)	Chloro paraffins Wax-naphthalene phenol condensates	0.1%—5°C	
Corrosion inhibitors (to prevent chemical attack on metal surfaces)	Phenols ; chloro acetoni- trites Amines Higher organic acids alkyl ammonium acid phosphates (Benzyl phosphates)	0.4—2%	
Anti-bearing corrosives	Hydrazides, zinc dialkyl dithiophosphate sulfuris- ed terpens	0.5%	

TABLE—2.11 (Contd.)

Purpose	Additive	Quantity	Ref :
Antiwear improvers (For protection of surfaces of high friction by forming protective films)	Fatty acids, dibenzyl disulfide, Tricresyl phosphates*		
Detergents (Clean surface exposures and eliminate deposits) keep oil insoluble material in suspension.	Organometallic compounds, Soaps of Ca, Mg, Ba, etc. Poly amines or sulfonates	2 to 10%	
Dispersants (to keep sludges in suspension and not allowing them to deposit)	Organometallic compounds of Ca, Sr.		
Anti foams	Silicones	f 0 001%	
Rust preventors (prevents rusting even in presence of moisture)	Soaps of fatty acids ; Metal sulfonates		
Viscosity index improvers (improve viscosity temperature relations)	Poly olefins, ^d Styrene polymers Acrylate polymers		

TABLE-2.11 (Contd.)

Purpose	Additive	Quantity	Ref :
Oiliness (to improve thin film characteristics)	Vegetable and animal oils		
Extreme pressure agents (when heavy loads, and shock loads are encountered)	Esters of fatty acids, sulfonic acids ; sulfurised molybdenum esters Penta erithritol oleates and Bisphosphoramides, dichloro, dibenzyl disulfide lead naphthenates.		
Water repellants (Settle water from oil phases)	Long chain fatty acids, silicones ; boron compounds or hydrophobic polymers	200-2000 PPM	
Emulsifiers (when emulsions are required).	Sulfonates, naphthenic acids, mono alkyl amino borates, Lithium soaps.		

TABLE—2.12
ADDITIVES SUPPLIED BY DIFFERENT COMPANIES

Gasoline anti-oxidants :		Chemical	Quantity	
Ethyl Corporation	701	2, 6, di, tert, butyl phenol	1-4 Kgs/1000 Barrel	
Dupont	AO-5	<i>n-n</i> butyl-p-amino phenol	1-5	-do-
Lubrizol	803	2, 6 di-t-butyl p-cresol	2.5 to 10	-do-
Amoco	533	2, 6 di-t-butyl p-cresol	2.5 to 15	-do-
UOP	No. 85	dioctyl-p-phenylene diamine		
<i>Metal deactivators</i>				
Dupont	D M D	N, N' disalicylidene 1, 2 diamine propane	0.1 to 1.5	-do-
Lubrizol		-do-	0.4 to 1.2	-do-
Ethyl Corporation	M D A	-do-	0.2	-do-
<i>Corrosion inhibitor</i>				
Dupont	AFA-1	alkyl amino		
Petrolite Corporation	KONTROL-157	alkyl phosphate Not known	0.5 to 10 —	-do-
<i>Ignition Controls</i>				
Amoco	541	Phosphorus Compounds	0.2-0.4 T	
Ethyl Corporation	KC-1	Bis-thiono phosphate	0.2 T	
	ICC-4	Tery methyl phosphate	0.2 T	
Monsanto	CDP	Gresyl diphenyl phosphate	0.2 T	
(T : theoretical requirement to convert lead in gasoline to Pb ₃ (PO ₄) ₂)				
<i>Detergents :</i>				
Amoco	572		2.5 to 12.5 Kgs/1000 B	
Lubrizol	580		1.75	-do-
Anticings	Dupont	DMF	Vol. % .02 to 0.1	

TABLE—2 12 (*Contd.*)

	Chemical	Quantity
<i>Multifunctionals</i>		
Dupont	Amine salts of alkyl	2.5 to 10 Kgs/1000 B
DMA-4	phosphates	
DMA-5	DMA-4 plus cresyl	5 to 45 -do-
	diphenyl	
	phosphate	
<i>Biocides</i>		
Phillips		200-1000 PPM
PFA 55 MB	Biobar JF	135-270 PPM
Sohio		

2.3.9.4. Copper Corrosion Test

The use of copper in electrical industry is immense, hence the attitude of oil towards copper should not be calamitous. Satisfactoriness of oil can be verified by heating a copper strip in oil for 3 hours at 100°C and observing the copper strip. Discoloration of the strip is direct indication of corrosiveness of the oil as given below :

Appearance of Sample (Copper strip)

Light Orange, looks like a fresh one	— (1)
Dark Orange to red or multi coloured	-- (2)
Multi coloured with greenish tinge	— (3)
Dark grey to black colour	— (4)

International Electro Technical Commission (IEC) test involves the blowing of air through oil at 150°C for 45 hours in presence of copper strip. After oxidation, the oil is tested for acidity and sludge.

Indian specifications of transformer oil is given below :

1. Sludge value (Heptane by wt)	1.2% Max
2. Acidity mg KOH/gm after oxidation for 164 hrs at 100°C	0.4 K(OH)/gm (fresh) 2.5 Max
3. Electric strength one min.	40 K.V.
4. Saponification value mg KOH per gm in oil	1.0 Max
5. Acidity gm KOH/gms of oil	0.03
6. Viscosity at 27°C CS	27 Max
7. Pour point °C	—10 Max
8. Flash point °C (Pensky Martin Apparatus)	140 minimum
9. Copper strip corrosion (at 100°C for 3 hrs)	Not more than 1
10. Resistivity at 90°C ohms cms at 27°C	13×10 ¹² min 500×10 ¹²
11. Specific Gravity	0.89 max

2.3.10 BITUMEN

Bitumen is the residual product obtained from crude distillation unit. It is essentially solid at room temperature and has got very high viscosity. Asphalt is usually a mixture of bitumen in oil, containing much mineral matter. Bitumen natural deposits are also available; famous Trinidad pitch lake is such a deposit. Bitumen obtained from the distillation column is poor in qualities. This has necessitated air blowing of bitumen to obtain suitable grades. Most of the bitumen is used in high-way constructions, waterproofing and coatings works.

Bitumen is specified by the following two tests

- (a) Softening Point
- (b) Penetration index.

These two tests do not describe the properties of bitumen completely. Other tests like viscosity, volatility, durability, ductility are necessary for obvious reasons. Outlines of these tests and significance are mentioned below :

2.3.10.1 *Softening Point (ASTMD 1398 IP.198 Ball & Ring test)*

Bitumen being amorphous does not melt sharply. The softening point is found out by the Ball & Ring Test. Bitumen is first melted and casted into discs of two numbers in standard rings. A steel ball weighing (3.5 ± 0.05) gms (dia 9.53 mm) is kept on each casted disc of bitumen. The whole stand carrying these two discs with balls is immersed in a water or glycol bath. As the heating proceeds, softening occurs. The temperature at which the sample detaches from the die and falls; indicates its softening point. The two samples from such rings are supposed to fall within a difference of 5 seconds. Higher the softening point, the better is consistency of bitumen. (See Fig. 2.24).

2.3.10.2 *Penetration Index*

The hardness or penetration quality of bitumen is assessed by this test (IP 49/72).

A standard needle is allowed to penetrate under a load of

100 gms, through a sample kept at 25°C for 5 sec. Distance travelled under those conditions indicates the consistency of

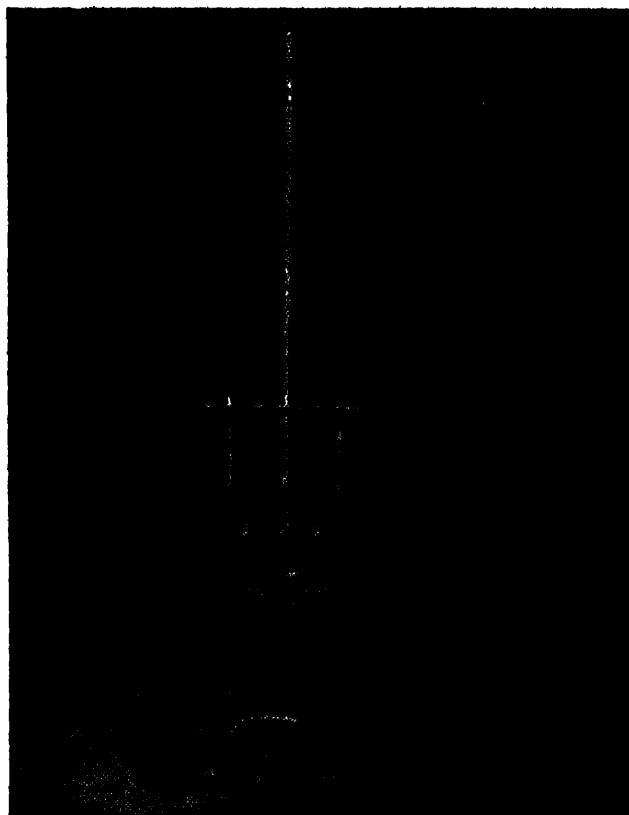


FIG. 224. Smoke point apparatus

sample. The distance (easily) travelled would naturally depend upon its load, and softening point. More penetration index naturally impairs the surface applications, where hardness is sole criteria.

2.3.10.3 Ductility (D 113)

Bitumen must possess good ductility, when it is used in surface application. The ductility is measured by a ductilometer. Ductility is a measure of the capacity of bitumen to elongate or stretch. This test is carried out by pulling a test piece of bitumen of standard dimensions at a uniform rate (5 cm/min) keeping sample at 25°C. Higher capacity for elongation indicates that the sample is having a high ductility.

Other tests like viscosity, boiling point, ash content are

desirable. Suitable solvents are added to solubilise the bitumen and then applied over the surface, when the solvent evaporates a fine layer of bitumen appears. These type of bitumens are called cutback bitumens. These cutback bitumens, after full curing period must possess the same properties as the bitumen from which they are made.

Indian specifications of bitumen are given below :

BITUMEN
IS SPECIFICATIONS

Grade	Sp. Gr. 27°C	Flash point °C min.	Soft point °C	Penetration	Ductility cm min	Solubility in CS ₂ % max
75/15	1.0 —1.05	200	65—80	10—20	25	99
65/25	"	"	55—70	20—30	10	99
75/30	"	"	70—80	25—30	3	99
85/25	"	"	80—90	20—30	3	99
85/40	"	"	"	35—45	3	99
90/15	1.0 —1.06	"	85—100	10—20	2	99
105/20	"	"	95—115	15—25	2	99
115/15	1.02—1.06	"	110—120	8—20	2	99
135/10	1.02—1.07	"	130—140	7—12	1	99
155/6	1.02—1.07	"	150—160	2—12	0	—

Grade 75/15 means softening point 75°C and penetration index is 15.

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PROBLEMS

1. Draw the ASTM distillation plots of marketted gasoline and kerosene. Convert these plots into EFV lines at atmospheric pressure and see whether there is any continuity, if not find the overlap.

2. (a) From the given data, draw TBP graph and asses the qualities of different fractions.

(b) Convert TBP curve to E F V curve for the above crude at 150 kg/cm².

Java, Indonesian crude

API : 28.8

P.Pt : 41°C

Sulfur wt : 0.11%

Vis. cs.

60°C : 56.1

45°C : 128.1

Sal Kg/1000 bbl : 70

Wax. wt% 23.8

C.R. 8.1%

Light naphtha

C₈-100°C : 2.6% by vol.

Sp. grv. 0.701

Paraffins%	62
Naphthenes%	30
Aromatics%	8
RON	70

Naphtha

100–155°C	3.0% by vol.
sp. gr.	0.755
Paraffins%	46
Naphthenes%	43
Aromatics%	11

Kerosine

155–295°C :	13.4% by vol.
Sp. gr.	0.813
Aromatics vol. %	15.5
Sulfur wt.	0.04%
Smoke point	19

Heavy distillate

295–350°C	7.3% by vol.
Sp. gr.	0.834
P. Pt.	15.6°C
Diesel index	72
Catane no.	66
Sulfur wt. %	0.08
Viscosity(CS) at (38°C)	— 5.53

Residual oil

More than	350°C · 72.9% by vol
Sp. gr.	0.915
P. Pt.	58°C
Sulfur wt. %	0.12
Vanadium Nickel Iron PPM	1.6/0.6/24
Viscosity at 80°C	280 (cst)

3. (a) Estimate the gross calorific value of a kerosene fraction having an API gravity of 48 from eq. 2.13.

(b) Estimate the heat energy required in raising the temperature from 35°C to 82°C. The fraction has a cubic arrange boiling point 204.5°C. (use eq. 2.11 and Fig. 2.6(a))

(c) If this fraction were to vaporise completely, find the specific heat of fraction in vapour phase (use eq. 2.12).

4. A natural gas having a calorific value of 43.4 MJ/M³ and density of 0.632(gms/lit) is allowed to burn at 5 milli bars ; a replacement with another gas of 25 Wobbe number is sought. Find the pressure at which the gas should be combusted ?

5. 3000 kilo liters of gasoline of 74 API has to be stored in a tank of suitable capacity under varying temperatures of a maximum fluctuation 22°C. Assuming an average temperature of 25°C design a suitable storage tank. Find the breathing losses.

6. (a) 150 Neutral oil, is having a viscosity of

$$\frac{134 \text{ SSU/at } 38^{\circ}\text{C}}{(28.8 \text{ cs/})} \text{ and } 42.4 \text{ SSU at } 99^{\circ}\text{C}$$

Find the viscosity index (consult 1P tables for getting standard value of L & H).

(b) From its VGC value classify the nature of oil (API gravity 30).

7. Estimate the viscosities of toluene and ethylbenzene, by Souder's method at 25°C.

8. Find the vapour pressure of a chlorinated methane at 120°C using Claussius—Clapeyron equation.

B.P. 76°C.

Latent heat of vaporisation at boiling point : 7140 Cals per gm mole
(Ans : 1440 mm Hg)

9. Vapour pressure of a hydrocarbon is represented by the following eqn. $\log P(\text{atm}) = \frac{-314.49}{T^{\circ}\text{K}} + 8.05$

Calculate the latent heat at one atmospheric pressure and boiling point 165°K (neglect liquid volume).

(Ans. 1200 Cals/g.mole)

10. The thermodynamic properties of a paraffin gave the following values at 32°C and 3 Kg/cm².

Density of liquid = 0.5635 gm/cc.

Density of saturated vapour = 0.00756 gm/cc.

Latent heat of vaporisation = 85.2 gm cals/gm.

The vapour pressure as a function of temperature was found to be represented by the equation

$$\log P(\text{atm}) = a + \frac{b}{T} + 1.75 \log T + CT$$

where $T = ^\circ\text{K}$

$$a = 1.756$$

$$b = -1337.8$$

$$c = 0.004$$

with the aid of Clapeyron equation test the consistency of the above relation.

11. Explain how ATF differs from aviation gasoline. What are the additives required for a good ATF ?

12. (a) What are the different additives used in gasoline and diesel oils ?

(b) Explain the effects of paraffin rich fuel in spark ignition engine.

TABLE 2.4

RELATIVE EQUILIBRIUM VOLATILITY LOSSES OF GASOLINE OF RVP : (0.6 kg/cm²)

Sl. No.	Relative losses at 38°C (b) (Sea level)	Altitude (Meters)	Atmospheric pressure (a) N/sq.m ²	Temp. °C	Losses at altitude and ambient temp.
1	2.55	1,800	81,000	3	2.22
2	3.63	4,600	57,000	-14.7	3.02
3	6.27	8,500	33,000	-40	4.64
4	13.79	14,000	15,000	-50	10.12

(a) Ernest E. Ludwig, *Applied Process Design for Chemical and Petrochemical plants (GPC)*.

(b) Taken loss at sea level and 30°C as 1%.

evaporation. This has been to some extent been alleviated by fixing vapour pressure, which is furnished by entire boiling stock. Further, evaporation losses can also be related to vapour pressure. When gasoline tanks are filled up, the vapour that occupied the tank has to be displaced and losses due to such kind of phenomenon are called 'breathing losses' which are inevitable in all filling operations. Breathing losses are in addition to evaporation losses due to ambient temperatures. (Table. 2.4) with all these considerations, to ease starting, winter gasolines and summer gasolines are produced to satisfy the seasonal specifications. Rate of acceleration follows after the starting operation which is best judged by the mid region boiling range (say 30-60%). Rapid warmup is not very essential. It is generally influenced by prevailing weather conditions. Warmup period is defined as the time required to develop fully the engine power. Usual running of engine to 6-8 Km, should be a well considered warm up period and this is closely governed by % distilled at 70°C, with reference²⁶ to minimum ambient temperature as shown below :

% Distilled at 70°C	3	11	19	28	38	53
Minimum ambient temp. in °C	26.7	15.6	4.4	6.7	-17.8	-29

This explains that 11% should be distilled at 70°C, if the ambient temperature is 15.6°C, for maintaining the required warm up. Evaporation losses and vapour locking are guided by RVP and ambient temperatures, as shown below :

Ambient Temp., °C	15.6	21.1	26.7	32.2	37.8	43.3	48.9
Max. RVP (lbs/in ²)	12.7	11.0	9.4	8.0	7.0	6.0	5.3
(kgs/cm ²)	0.879	0.782	0.66	0.56	0.496	0.423	0.38

ASTM distillation curve closely reveals the following :

If 10% boiling point is low ; then

Flash point,	— low
Ease of starting,	— excellent
Vapour losses,	— very high
Vapour locking,	— high

30-60% boiling point range gives information on

- (a) Warm up period (b) Good evaporation

If the range of boiling point is high gasoline will not be evaporating normally. If 90% boiling is high, then crank case dilution also increases as the fuel is not volatile at the working conditions of carburettor (Fig. 2.16).

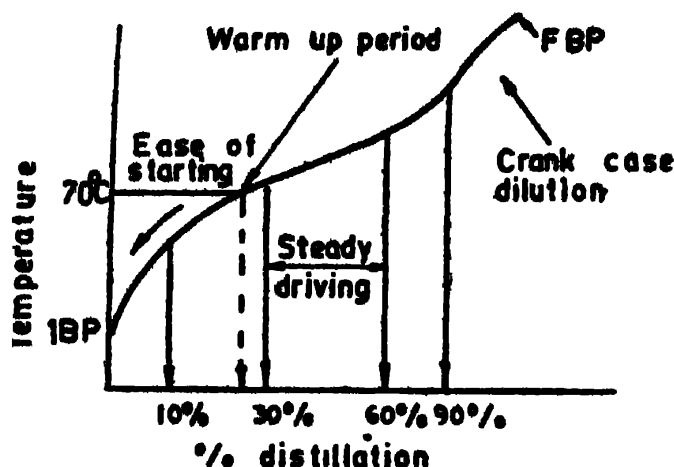


FIG 2.16 ASTM Distillation Characteristics

2.3.2.2 Reid Vapour Pressure (IS : 1448-39)

Vapour pressure of all volatile fractions is measured by the above apparatus at $(38^{\circ} \pm 0.1^{\circ}\text{C})$. The apparatus consists of two chambers. The lower chamber is in the form of cylindrical bomb for holding the test sample. Above this, there is air chamber which is a hollow cylindrical space, designed to possess four times the bomb volume. The top portion of the chamber is fitted with a bourdon gauge for pressure indication. For the test, the bomb is first filled with the sample up to the brim and immediately the valve is closed and connected to the air chamber. The apparatus is now immersed in a water bath kept at $38^{\circ} \pm 0.1^{\circ}\text{C}$. The maximum pressure indicated by the gauge is counted as the Reid vapour pressure of the sample. LPG, gasoline, naphthas, jet fuels are tested like this. It is found that true vapour pressure in most of the cases is higher than the indicated RVP, and the variation for different fractions is different. Maximum difference is indicated in case of crude oils. Relative expression 'True vapour

pressure to RVP' is also sometimes indicated and for gasolines it is in the range of 1.03 to 1.45, while for crudes it goes upto 10.

During testing, the following correction is applied for accommodating the changes in water vapour pressure corresponding to temperature variation from air to bath temperature.

$$\text{Correction : } \frac{(P_a - P_s)(t - T)}{T \cdot K} - (P_T - P_s)$$

where, P_a —atmos. pressure, P_s —vapour pressure of water at $t^\circ K$, t —air temp. $^\circ K$, T —Temp. at which test is done $^\circ K$, P_T —vapour pressure of water at $T^\circ K$.

Volatility tests are intended for smooth performance of engine under all weather. The importance can be judged by U.S. Volatility.

TABLE 25
U. S VOLATILITY TRENDS OF GASOLINE

	Regular				Premium			
	Winter 1956—1966		Summer 1956—1966		Winter 1956—1966		Summer 1956—1966	
Reid vapour pressure	0 773	0 822	0 605	0 633	0 773	0 836	0 619	0 639
10% Evaporation Temp $^\circ C$	47 3	43 3	53 9	51 7	46 8	43 3	53 3	51.7
50% Evaporation Temp $^\circ C$	100	93 3	104	97 9	98 4	98 9	103 6	102

2.3.2.3 Octane Number

Octane number is defined as percentage volume of *i*-octane (2, 2, 4-trimethyl pentane) in a mixture of *i*-octane and *n*-heptane that gives the same knocking characteristics as the fuel under consideration. Knocking is due to untimely burning of fuel in a spark ignition engine, which results in loss of power and sometimes it is powerful enough to cause damage to engine parts. With the advent of petrol engines of high compression ratios the tendency of knocking has also increased. Knocking

is mainly due to two reasons, one assigned to engine and the other to fuel. The fuel part is only dealt here. Being a blend, gasoline responds in different ways, even in the same engine, depending upon the components present. Iso-paraffins and aromatics have high octane numbers while *n*-paraffins have very low value (heptane 0), unsaturates do have high octane values but not preferred due to gum contribution. Naphthenes usually lie in between *i*-paraffins and aromatics. Even among *n*-paraffins also the octane number of the lower carbon series is very high (methane has 104) and that is the reason why natural gasolines or LSR (C_5 -100°C) have high octane ratings. Octane number is influenced by different factors like speed of the engine, ambient weather conditions, altitude, combustion chamber deposits and coolant temperature.

Knock rating is tested by CFR Engine for different purposes and the conditions of test are furnished below.

Method	Research	Motor	Aviation	Aviation supercharge
Designation CFR	F ₁	F ₂	F ₃	F ₄
Engine rpm	600±6	900±9	1200±12	1800±45
Air intake °C	75±1	38±1.4	75±2	75±2
Coolant temp. °C	100±1.5	100±1.5	140±5	140±2

Motor method (P. 26, ASTM D357-58) gives the octane rating of high way driving (high speeds), while research method (P. 27, D 908-58) gives for city driving (low speed) conditions F₁ & F₄ methods are for aviation gasolines.

Some additives like tetraethyl or methyl lead are extensively blended into gasolines to boost the octane number.

Octane number estimation for leaded gasolines was furnished by McCoy²⁷ as

$$\text{Octane number} = A(\% \text{ aromatics in fuel}) + B$$

where A & B are constants.

After analysing vast data, the above relation was formulated. The octane number variation with aromatics resulted in a straight line and A and B are the slope and intercept of such a line.

Ambient conditions—Octanes²⁸ number :

Any engine during service has to encounter different weather

conditions. For smooth running it is better to adjust the octane rating of the fuel under such circumstances.

Altitude : With increasing altitude a fuel of less octane value is satisfactory. For every 100 meters increase in altitude drop of one unit RON in fuel quality is allowed.

Humidity

The performance of the engine is again responsive to humidity conditions. Engine working on high humidity conditions require less octane fuel. For an increase of 10% humidity at 25°C a drop of 0.5 RON in fuel quality is permitted.

Engine Speed

High speed engines require low octane value fuel. For an increase of 300 RPM in an engine speed, a decrease of one unit RON of fuel quality is permissible.

Air temperature

Cold countries require less RON fuel than hot countries. With a rise of 12°C in air temperature, an increase of one RON in fuel is required to compensate the effect of air intake temperature.

Coolant temperature

For every 6°C increase in coolant temperature, the engine demands an increase of one RON in quality of fuel as essential. By this one can judge the importance of coolant.

Spark advance

This is purely a mechanical adjustment requiring 1.5 RON increase for 1° advancement of sparking.

Combustion chamber deposits

Running of an engine over sufficiently long periods, invariably results in deposits. It is essential to increase the octane number of fuel by one unit for 5000—10000 km of running.

Alkylated gasolines and reformed (catalytic) gasolines have high octane numbers. While polymer gasolines contribute to medium extent (60-80) RON, gasolines produced by cracking and hydrocracking techniques yield about 60 RON. The light ends of any gasoline produced by thermal decomposition of higher

stocks give good value RON, still they are not preferred because of the large quantities of unsaturates.

2.3.2.4 *Oxidation—Stability (Gum content)*

Motor gasolines are often stored for six months or even longer before use. So it is essential that they should not undergo any deleterious change under storage conditions. Further gasolines should remain free from deposits during discharge from the fuel tank of a vehicle to the cylinder of its engine, otherwise these harmful deposits are built up in the tank, fuel lines and in valves and cause extensive choking. Gasoline manufactured by cracking processes contain unsaturated components which may oxidise during storage and form undesirable oxidation products. An unstable gasoline undergoes oxidation and polymerisation under favourable ambient conditions, forming gum, a resinous material. This in early stages of formation may remain in solution with gasoline but due to further chemical changes may be precipitated.

Gum formation appears to be the result of a chain reaction initiated by radicals such as peroxides and catalysed by the presence of metals, particularly copper, which might have been picked up during refining and handling operations.

This deterioration of gasoline can be eliminated for a substantial period of time by addition of small quantities of antioxidant additives known as inhibitors. Inhibitors retard the oxidation of the olefin constituents of the fuel. Some such inhibitors are normally phenols or amine compounds, and small quantities between 0.001 and 0.02 percent by weight are usually sufficient to ensure good stability.

Gum is of two kinds, one is known as existent-gum (pre-formed) while the other is called potential gum (ultimate). These two gums are estimated by two different methods. Existent gum, as already available in solution, is to be separated by evaporation of the volatile gasoline. This is estimated by ASTM D381; IP 131 test. In this test, a sample of 100 ml. is evaporated with the aid of a heated jet of air, while the sample is maintained at 160-166°C. After the evaporation of the sample the residue is weighed. Usually gum content should not exceed 6-10 milligrams per 100 ml. of gasoline.

Potential or ultimate gum content of the gasoline is evolved by oxidising the sample with oxygen under restricted conditions, thus assessing possible gum formation during storage.

Induction period for gum formation is estimated by Bomb method (ASTM D525 ; IP 40 : P. 28). This employs an atmosphere of oxygen at initial pressure of (7 kg/cm²) over the test sample of 100 ml. in a specially designed bomb. The bomb is fitted with a pressure gauge for indication of pressure, another connection is provided for feeding oxygen. The bomb and its contents are kept in a water bath and heated continuously at 100°C till the test is over. Due to slow oxidation gum formation begins and the pressure of oxygen in the bomb slowly falls. The time required for fall in pressure by 0.15 kg/cm² within fifteen minutes is taken as break point. The difference in time from placement of the bomb to break point is the required induction period. More induction period means more the stability of gasoline, hence less chance of gum formation. A minimum figure of 240 minutes usually ensures satisfactory limit for storage. Induction period in hours is equivalent to months that the gasoline can be stored under commercial terms. Further, extent of inhibitor (additives) to be added is guided mainly by induction period.

2.3.2.5 Sulfur

In addition to corrosiveness and pollution, sulfur compounds are extremely harmful to the susceptibility of gasolines to tetra ethyl lead (TEL).^{29a} More TEL is required if sulfur components are present in gasolines. The effect of overcoming sulfur compounds is done by adding more ^{30' 31} lead. The effect of sulfur on lead can be predicted by the relation given as :

$$L = \frac{a_0 - a}{a_0} \times 100$$

where, a_0 = TEL present in gasoline with sulfur compounds

a = TEL present in gasoline, free of sulfur compounds,

L = % TEL excess required to boost the octane number of sour gasoline to the same extent as sweet gasoline.

Sulfur is also termed as noncorrosive sulfur, provided the sulfur exists in alkyl disulfide form only. Most of the sulfur in

crude is concentrated in heavier fractions, lighter fractions require relatively less cumbersome treatment techniques. Total sulfur is estimated by bomb method (1 P. 6/60, P. 33) or lamp method (P : 34) and mercaptan sulfur as silvermercaptide (P. 36 : IP 104/53).

2.3.3 ADDITIVES FOR GASOLINE

While modern gasoline engines have been designed for efficient use of gasoline, still, gasoline engine operation is not entirely trouble free. Complete combustion of gasoline in engine is rare. Motor oils used for lubrication cause deposits in the combustion chamber. These deposits (presumably of high carbon ring compounds) enter the crank case of the engine to form lubricating oil sludges along with unburnt gasoline. Other source of trouble is effluent through positive crank case ventilation which causes deposits in the delivery end of the carburettor. Thus a clean combustion is remote ; hence additives are preferred to reduce the deposits as well as pollution belches. The effect of sulfur in different forms on lead requirement is presented in Figs. 2.17a & b, c & d.

Different types of additives are blended into gasoline, in fact in all petroleum fractions, to give uninterrupted and smooth service. Additives for different functions are classified as follows :

1. Anti-icings and detergents
2. Inhibitors for (a) corrosion (b) oxidation
3. Combustion aids
4. Anti-knocks
5. Colours and dyes.

2.3.3.1 *Anti-icings and detergents*

During cold and wet weather, spark ignition engine has a tendency to stall till the combustion chamber is fairly warmed up. Formation of ice crystals begins when the ambient temperature is -5 to 10°C , at a relative humidity of 65%. This phenomenon is observed even when gasoline is free of moisture, so, obviously moisture is contributed by air. During vaporisation of fuel in carburettor, there is evidently a good temperature drop. These two facts result in uninvited formation of ice crystals. For prevention of these formations, additives like glycols mono ethers, methanol, propanol are added.

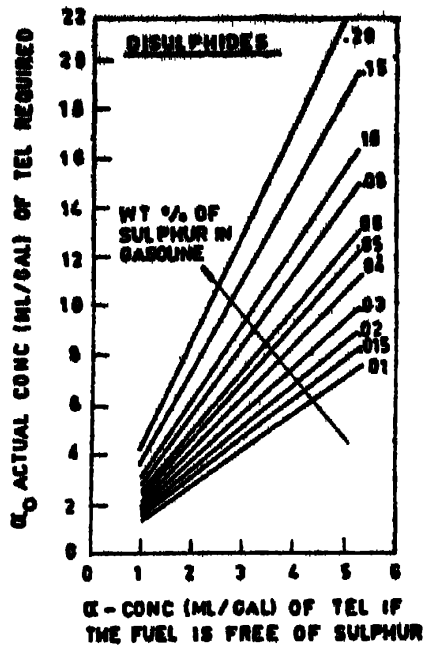


FIG. 217(a)

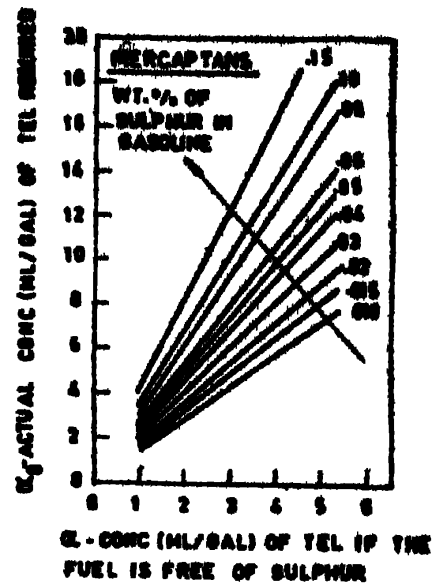


FIG. 217(b)

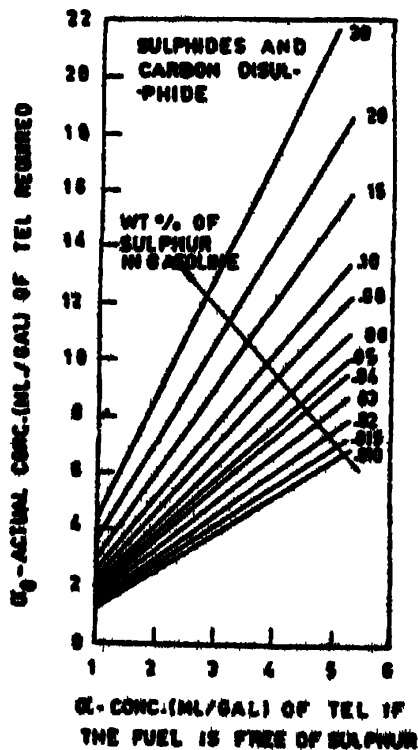


FIG. 217(c)

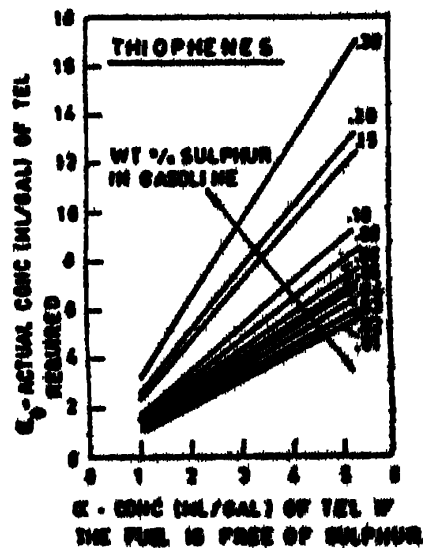


FIG. 217(d)

FIG. 217. a, b, c, d Effect of Sulfur Compounds on Lead Requirement

(a) Disulphides

(b) Mercaptans

 (c) Sulphides & CS₂

(d) Thiophenes

It is true, where moving parts are present a timely lubrication is demanded. Carburettor detergents take care of smooth function of carburettor. For free piston movements; rapid erosion of deposits in combustion chamber, lubricants and some scavengers are essential. The deposits are mainly due to decomposition of lube oils and carbon formations by frictional heat and combustion heat.

Maleic anhydride, polyamines, poly isobutylenes, phenol epichlorohydrin—amine products are some such detergents in service. As an example phenol—aldehyde amine condensate products reduce the deposits by 73% just by addition²² of 63 ppm. Petroleum sulfonates are cheaply available additives for smooth lubrication

2.3.3.2. *Inhibitors (corrosion)*

Storage and transportation of petroleum products is unavoidable. Rust prevention in these periods is essential. This is done by incorporating selective additives in products. These additives form a layer of coating on the metals and protect from rusting. Ammonium sulfonates, organo phosphoric compounds are such additives. Magnesium and silicon compounds are used for prevention of lead corrosion.

Oxidation inhibitors

Oxidation may be accelerated by metallic impurities like copper and its alloys unsaturates always have an inclination to react with atmospheric oxygen leading to gum formation. This is due to free radical mechanism. Hence the inactivation or termination of these free radicals ensures inhibition to oxidation. Anti-oxidants like phenols, cresols, phenylene diamines, alkyl amino phenols serve the purpose. Copper corrosion can be prevented by addition of disalcyledine and aminopropanes. Gasoline stabilised with *n*-oxydiphenyl amine was found to be without deterioration, even after two years²³. Without additives gasoline should not be stored for more than six months.

2.3.3.3 *Combustion Aids*

The deposits in the combustion chambers often glow and cause the fuel to burn untimely and contribute knocking. Boron com-

pounds²⁴ (organic) in small amounts not only decrease the combustion deposits but also increase the effectiveness of antiknock-ing agents.

Organo phosphorous compounds²⁵ can also reduce surface ignition by forming a refractory layer and preventing glows. Phosphates of lead, having higher glow temperatures, really impressed the manufacturers to go for high compression ratio engines.

2.3.3.4 *Anti-knocking Agents*

Tetraethyl lead is the most important of all the additives of gasoline. Though working mechanism is not convincingly reported, it is assumed to decompose into free radicals of organic nature and lead. The ions of lead try to stop the propagation of flame, thus establishing an instantaneous combustion, which favourably decreases the knocking effect, but pollution due to oxides of nitrogen increases. Further, lead compounds accumulate in engine parts. This has to be met by suitable scavengers like dibromomethane additive. With stringent pollution laws, refineries do produce unleaded gasolines of premium and regular grades. Tetramethyl lead is also employed in place of tetra ethyl lead. Modern tendency is to add a single suitable additive that can take care of all these additives. One such additive gaining importance is methyl cyclopentadienyl manganese tricarbonyl.

2.3.3.5 *Dyes*

Though dyes do not have special contributions towards gasoline properties, still they are incorporated for obvious reasons, namely to identify, to assess if there is any deterioration in gasoline during storage and to impart pleasing hues especially when cracked gasolines are blended. Pink colour is used for automobile gasoline, while light blue colour is added for aviation gasoline.

Quantities of Additives

Additive	Quantity
1. Antiknocks, TEL	0—3 ml/5 liters
2. Anti oxidants	1—8 kgs/1000 bbl
3. Metal deactivators (salicyledene)	0.5—2 kgs/1000 bbl
4. Corrosion-preventers	10—50 ppm
5. Preignition preventors/ Combustion aids	0.01—0.02%
6. Anti icing agents	1/2—1%
7. Dyes and colours	traces

The specifications of gasoline are shown in Table 2.6.

TABLE 2.6 SPECIFICATIONS : MOTOR GASOLINE, 83 RESEARCH

Sl. Characteristics No.	Method	Unit	Requirement
1. Colour	Visual	—	Orange
2. Copper strip corrosion for 3 hours @ 50°C	P : 15		Not worse than No. 1
3. Density @ 15°C	P : 16	g/ml	To be reported
4. Distillation :			
Initial Boiling Point		°C	To be reported.
Recovery upto 70°C, Min		%vol.	10
Recovery upto 125°C, Min		%vol.	50
Recovery upto 180°C, Min		%vol.	90
Final Boiling Point, Max		°C	215
Residue, Max		%vol.	2
5. Octane Number (Research Method), Min	P : 27	—	83
6. Oxidation Stability, Min	P : 28	Mints.	360
7. Residue on Evaporation, Min	P : 29	mg/100 ml	4.0
	(Air Jet Solvent Washed)		
8. Sulphur, Total, Max	P : 34	%wt	0.25
9. Lead Content (as Pb), Max	P : 37	gm/l	0.56
10. Reid Vapour Pressure @ 38°C, Max	P : 39	kg/cm ²	0.70

2.3.3.6 Aviation Gasoline

Gasoline used in aircrafts has more stringent specifications than motor spirit, although, it contains all the additives meant for motor gasoline. Sulfur content and paraffin content are more injurious to this fuel, as the operation under -60°C is severely hampered due to crystallisation of paraffin compounds. Sulfur is presumably kept below 0.05%, to eliminate the possible pollution and corrosion problems. With the advent of modern jet engines, the demand for aviation gasoline is gradually falling.

Cracked products in aviation gasolines are not permitted due to their chemical behaviour of giving inimical deposits, i-paraffins and naphthenes are preferred and form bulk of constituents. n-paraffins and aromatics follow. Aromatics (Max. 12%) are also not very much desirable (their presence is greeted very much in motor gasoline), as they do not possess high anti-knock characteristics under lean mixtures, but their performance is excellent during take off (rich mixtures). Iso octane and other alkylated products are in immense demand because they suit in close boiling ranges of aviation gasoline ($35-170^{\circ}\text{C}$) with high octane member.

All the tests needed for motor gasoline are well applied to this also. As a special case the sum of 10% and 50% ASTM distillation temperatures must not be less than 135°C . This is required to control excessive volatility. Final boiling point is kept in the vicinity of 170°C . Reid vapour pressure is less than motor gasoline and is kept around 0.4 to 0.49 kg/cm².

2.3.4 AVIATION TURBINE FUELS (ATF), JET FUELS

Modern jet engines use fuel similar to kerosene. It is a most flexible fuel in its boiling range (upto 300°C). All properties which are desirable for kerosene are considered to be sufficient. Pour point of this fuel is of extreme importance and should not be higher than -30°C as international flights always visit lands of caprice climates. High smoke point is essential for clean combustion. Smoke is contributed by aromatics and is made of high carbon to hydrogen ratio molecules called carboids which can be distinguished from coke. Naphthenes have good smoke point and illuminating characteristics, hence preferred in these fuels. To elevate the smoke

point, aromatics should be either converted to naphthenes or physically removed. It is thus required to keep aromatics in limits of tolerance upto 20%. Unsaturation estimated by Bromine number are kept below 5% to limit gum formation. Sulfur is fairly tolerated, unlike gasoline. Different aviation grades like JP—1, JP—2, JP—3, JP—4, JP—5 are used in U.S.A, while in India two grades K 43 and K 50 are produced. (See Table 2.7)

Smoke point is an important property of jet fuel. Sometimes instead of expressing the quality of jet fuel by smoke point alone, it is expressed in terms of smoke volatility index defined as

$$\text{Smoke volatility Index} = \text{Smoke point} + 0.42 \times (\% \text{ distilled at } 204^{\circ}\text{C})$$

The advantages gained by this expression are still not clear. The tests prescribed for this fuel are

- (1) Volatility (ASTM)
- (2) Pour point
- (3) Smoke point (combustion quality)
- (4) Water retention and separating properties

Volatility had already been discussed ; pour point and smoke point are discussed in the kerosene and lube oil tests.

Jet fuels being denser and viscous than gasoline, they tend to retain fine particles and droplets of water for a considerable amount of time. Although filtration system can remove fine particles, it is no use for water droplets, water droplets can be removed by either heating or adding demulsifying agents. Maximum permissible limits of impurities are for fine particles 1 mg/litre and moisture content 30 ppm. Free water in jet fuels can be detected by field kits like Esso-hydro kit, Mobil Moisture Indicator. The standard water reaction test (IP 289) is used as in the case of aviation gasoline. The clarity of fuel is measured by photo electric device.

Noticeable phenomenon during high altitude flights and at high speeds is that fuel gets charged. To disperse these static charges antistats are added.

TABLE 2.7

<i>Aviation Turbine Fuel</i>		
	Grade K43	Grade K50
Acidity in grains	Nil	Nil
Aromatic % vol. max.	20	20
Bromine number, max.	5	5
Colour Saybolt, min.	8	8
Copper strip corrosion 2 hrs. at 100°C. Not less than No. 1		
Distillation		
(a) I.B.P.	Not limited but to be reported	
(b) Recovery upto 20% by Volume	-do-	
(c) Recovery upto 20%	200°C minimum	
(d) Recovery upto 50% by vol.	Not limited but to be reported	
(e) F.B.P. max.	300°C	300°C
(f) Residue, % age vol. max.	2	2
(g) loss percent by vol. max.	1.5	1.5
Flash point min.	38°C	38°C
Cold test temp. max.	-40°C	-50°C
Residue on evap. max. mg/ 100 ml	3	3
Gum accelerated (16 hrs.) mg/100 ml. max.	6	6
Cal. value Cal/gm. (min.)	10167	1016
Density at 15°C	0.775 to 0.825	0.77! to 0.82!
Sulfur by vol.	0.005	0.00!
Sulfur, total, percent by wt.	0.02	0.2
K.V. at -17.8°C (CS)	6	6
Water reaction Change in vol. of ether layer max.	1 ml	1 m'

The paraffin rich fuels can allow micro organisms to survive, for this reason, when these fuels are allowed to be stored over great period, biocides are added. Other additives are also used as in the case of aviation gasolines. Additives and their functions are presented below :

<i>Additives</i>	<i>(Purpose) Quantity</i>
Poly sulphones	Antistats 1 PPM
Organic boron compounds	Biocides (20 PPM element boron)
Phosphoric compounds	Rapid combustion aids in ram jets (200 PPM)
Glycol, polyhydric alcohols	Anti icing agents upto 1%

For jet fuels adequate information has not been provided by smoke point alone; a better method is by prescribing luminometer number (ASTM D-1740). Satisfactory luminometer numbers for some grades are given as

$$\begin{aligned}\text{For JP}_1 &= 51 \\ \text{JP}_4 &= 60 \\ \text{JP}_7 &= 75\end{aligned}$$

Further, the smoke point of fuel can indicate the percentage hydrogen content of fuel²⁷ as shown by the relation

$$\text{H}_2\% = 12.99 + 0.04 \times (\text{smoke point in mm})$$

2.3.5 NAPHTHAS

These fractions are highly volatile and fall in the boiling range of motor spirits. These are mostly used as solvents in paints, perfumery and other industries. Solvent grades are produced by distilling wide cut naphthas into small boiling range cuts. Naphthas are not suitable for combustion, because of the rapid flame propagation, resulting in explosions. Cuts boiling below 80°C do not have any aromatics, hence their solvent power is also less. Such fractions are sent for cracking operation. 80-120°C fraction is reformed to improve octane number and this goes as a blend into straight run gasolines.

General requirements of solvent naphthas are

1. Almost water white in color
2. Non-corrosive nature

3. High stability
4. High solvent power (Kauri Butanol test ASTM D1133)
5. Low boiling point
6. Low acidity

Suspended impurities are removed by filtration. Solvent power is determined by Kauri Butanol number. The volume of solvent that cause a standard Kauri Butanol gum in butyl alcohol to become a 10 point type illegible when viewed through this solution. Another method of estimation of solvent power is by Aniline point. Harvey^{29a} Mills relationship for KBN is given by

$$\text{KBN} = 99.6 - 0.806 G - 0.09912 A + 0.0755 (340 - B \times 0.56)$$

(For less than 50)

where $G = \text{Sp. Gravity}$

$A = \text{Aniline point, } ^\circ\text{C}$

$B = \text{Mid boiling temperature } ^\circ\text{C}$

2.3.6 KEROSENES

Kerosene is the general name applied to the group of refined petroleum fractions employed as fuel and illuminant. All these fractions have approximate boiling range 150—250°C. These are uniform close cut distillates, low in viscosity, with a good degree of refinement to be fairly stable, light in colour and free from smoky ill smelling substances. It is highly desirable that sulfur be kept as low as possible. Kerosene is used as illuminating oil in domestic needs both in wick burners and mantle burners. Though obsolete these days, it was used in railway signalling purposes. Such kerosenes were special blends of relatively high boiling fractions with oils of marine animals.

Tests and properties of kerosene :

1. Flash point and Fire point
2. Smoke point (Burning quality)
3. Volatility
4. Sulfur content
5. Aniline point

Above listed properties are cardinally judged for kerosenes of all grades. Specifications for superior kerosene are given in Table 2.8.

TABLE 2.8
SPECIFICATIONS KEROSENE (SUPERIOR)

Sl. No.	Characteristics	Method	Unit	Requirements
1.	Acidity, Inorganic	P : 2	mg KOH/gm	nil
2.	<i>Burning Quality</i> : Char Value, Max Bloom on Glass Chimney	P : 5	mg/Kg of oil consumed	20 Not darker than grey 21
3.	Colour (Saybolt), Min	P : 14		21
4.	Copper Strip Corrosion for 3 hours. @ 50°C	P : 15		Not worse than No. 1
5.	<i>Distillation</i> : Recovered @ 200°C, Min Final Boiling Point, Max		% vol. °C	20 300
6.	Flash Point (Abel), Min	P : 20	°C	35
7.	Smoke Point, Min	P : 31	mm	20*
8.	Sulphur, Total, Max	P : 34	% wt	0.25**

* For supplies to Defence, the smoke point of product shall be 21 mm minimum

** For supplies to Defence, the total sulphur, per cent weight, shall be 0.20 maximum.

2.3.6.1 *Flash point*

This is defined as the minimum temperature at which the vapours from oil sample will give a momentary flash on application of a standard flame under specific test conditions. Abel (P : 21 ; IP 170/59) Pensky-Martens (P : 21 ; IP 34/58) Cleveland are the test apparatus frequently used for the purpose. Significance of the flash point is that it can predict the possible fire hazards during transportation, storage and handling. Early tendencies were to incorporate more volatiles in kerosenes, thus inviting unusual fire hazards. This necessitated a strict vigilance by way of fixing flash point. The flash point of marketable kerosene should be above 42°C.

Pensky-Martens Apparatus (P : 21 ; IP 34/58) and Test :

The apparatus consists of a cylindrical cup made of brass of approximate dimensions $50.8 \pm 1.27 \text{ mm} \times 55.88 \pm 1.27 \text{ mm}$ (height inside) with a thickness at the bottom $2.41 \pm 0.64 \text{ mm}$. Inside the cup at $2/3$ rds height from the bottom there is a sudden and slight tapering up to the top of the cup. This looks like a ring and guides as a filling level for the sample. The top position acts as a vapour-air chamber.

This cup is provided with a lid, and the lid is actually made of two metal discs, one sliding over the other. The lid also includes (a) stirring device (b) two flame-holders, one test flame and other pilot flame (c) provision for thermometer (d) spring handle. By turning the spring handle, it is possible to slide one lid over the other whereby the exactly cut chords align with each other, exposing air-vapour mix of the cup to flame. In fact, there are three chord openings, central one is meant for flame introduction, while the other two act as air introducers. When the handle is turned test flame is also simultaneously lowered into the central chord opening to explode air-vapour mixture. The test flame is issued from an opening of 0.69 mm dia. The whole cup is heated by air-bath, which is primarily heated by electric power.

The test sample is filled up to the mark, and the temperature of the oil is slowly and uniformly raised at a rate of 3°C per minute. Test and pilot flames are lighted. Occasional stirring is done. The spring handle is rotated at every 1°C raise in thermometer; till a bluish light flash is noticed. Heating should be maintained at the prescribed rate.

Abel flash meter is used for highly volatile samples, whose flash point shall be less than 40°C . Pensky-Martens closed cup can be used for medium flash liquids, when a high flash point liquid is to be tested open cup flash meter is convenient.

Flash point is essentially dependent up on the light end characteristics of a fuel. Approximate relationship between flash point and IBP -10% boiling range is given by Nelson²⁰⁰ as

$$\text{Flash point} = 10.92 (T^\circ\text{C}) - 79.52$$

Flash point is regarded as vapour property hence the ambient pressure directly influences the flash point. Thus one is reminded to note the ambient pressure before such a test is conducted. Cor-

rection for pressure may be accorded by applying the following relation :

$$\text{Flash point } T^{\circ}\text{C} = \text{Flash point } (t^{\circ}\text{C}) \text{ at } 760 \text{ mm. Hg} + \frac{760 - P}{30}$$

where P is the pressure in millimeters at the time of observation. Flash point of blends does not follow any linearity : however the influence of high volatiles (range of 0—10% distillation) is predominant. Instead of laborious theoretical correlations it is always easy to determine the flash point of mixtures experimentally as shown in Fig. 2.18.

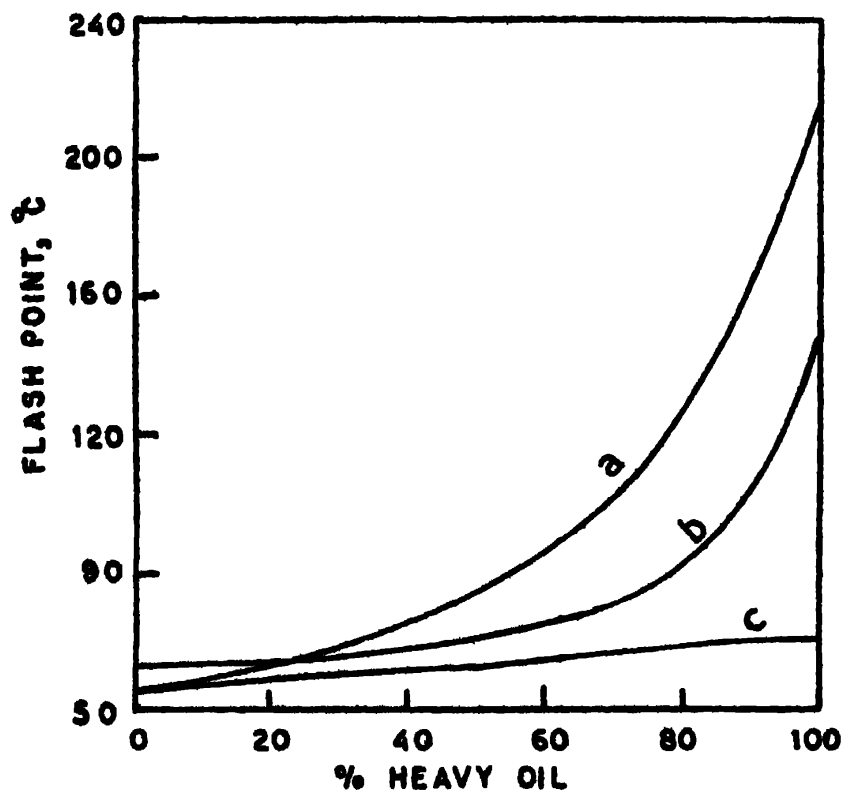


FIG. 2.18. Flash Point of Blends. a, b, c Curves show different blends of heavy and light oil

2.3.6.2 Fire point

This closely follows the flash point. The test is carried out in open cup rather than a closed one. Cleveland apparatus (ASTM D 92) offers the advantage of open flash point and fire point. Fire point temperature is noted when the oil vapours can burn continuously for 5 seconds when tested in flash point apparatus and it occurs after the flash point, by 3-4°C. For domestic

needs a very high flash point above 50°C is also not desirable. The easy ignition is credited to volatiles only and decrease in volatiles enhances the flash point causing difficulty in ignition.

2.3.6.3 *Smoke point*

Smoke point is an indication of clean burning quality of kerosene. Illumination depends upon the flame dimension although it is not related to flame height. Many paraffins may be gifted with better flame heights but illumination may be poor. Smoke point is defined as the maximum height of flame in millimeters at which the given oil will burn without giving smoke. Thus smoke point test (P : 31, IP 57) enables the burning quality to be measured by adjusting the wick height to give proper non-smokey flame (Fig. 2.19). Illumination is supposed to be characteristic of the components of fuel usually not measured. Different flame heights are obtained due to the presence of different components such as paraffins, naphthenes and aromatics.

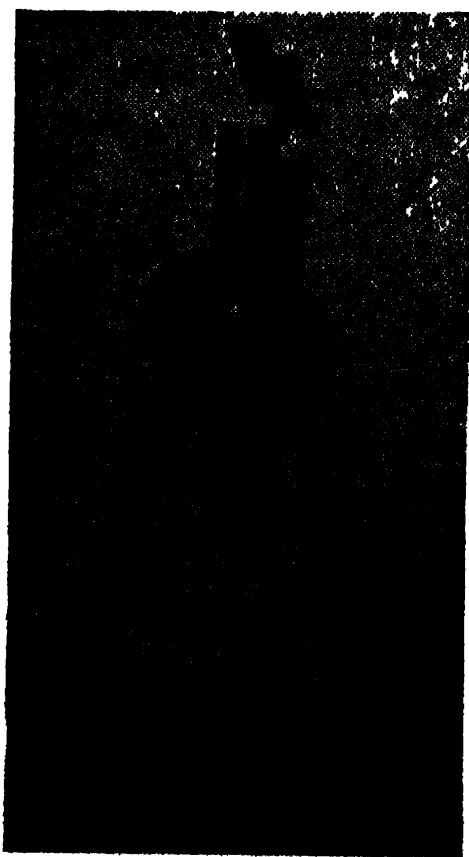


FIG. 2.19. Smoke point apparatus

Aromatics contribute smoke, hence removal of aromatics increases the smoke point. Naphthenes with side chains one inevitably retained to give good illumination. In Ind'a, marketable kerosene should possess a smoke point 18 mm. Smoke point may be predicted approximately by knowing the group composition of oil. given as :

$$\text{Smoke point} = 0.48 P + 0.32 N + 0.20 A.$$

where P, N, A are % of paraffins, naphthenes and aromatics in the sample.

A dogma of high smoke point meant a better quality fuel is not always acceptable as it can not specify any illumination characteristics. In recent literature stress is given to this luminosity number (ASTM D 1740) and prescribed as a test for kerosene. This indicates luminosity of the flame and accompanying radiation problems in combustion chambers. Smoke point apparatus with modifications to include a photo electric cell can measure the flame radiations. Luminosity number is expressed just like octane number. The constituents taken here are tetralin (0 luminosity number) and iso octane (100 luminosity number). The blend of these two should match with the luminosity of fuel.

2.3.6.4 *Burning Quality Test* (P : 5 ; ASTM D182)

This indicates the ability of kerosene to burn steadily and cleanly over a long period. Kerosene is tested by burning in a standard wick lamp for a period of 24 hours, in a room free from air currents. The average rate of burning, change in shape of flame, the density of chimney deposits are the prime factors by which the quality of kerosene is assessed. A good quality kerosene (after burning for 16 hours) should present the chimney as clean as possible (only slightly clouded) and the wick should not have any appreciable hard incrustations with as large flames as in the beginning.³⁰

The continuity of the initial illumination over long periods in a lamp rests on the normal flow of kerosene to the wick end. Quantity of oil available at the tip of wick depends on the height

of wick over liquid surface, texture of wick and properties like viscosity and surface tension of oil. Even though surface tension of different oils (kerosenes) may not vary much, viscosity varies. Stabilisation of flame is governed by viscosity. A good oil of 650 c.c must burn at least for 120 hours.

2.3.6.5 *Volatility*

The nature of distillation range estimated by ASTM D 86 is of significance with regard to burning characteristics. Ten percent boiling point reveals the flash point which in turn, indicates the ease of ignition ; specially when kerosene is used in pump stoves, this plays a very important role in continuous support of flame. Mid boiling range contributes towards viscosity. Often flare up in oil heaters is observed if mid-boiling range is not properly constituted. Sixty percent distillation at 200°C ensures steady performance of oil in heaters. Minimum of 15% distillation at this temperature is enforced to guarantee adequate volatility^{41a}.

2.3.6.6 *Sulfur content*

High sulfur content is inimical due to its combustion products. When large amounts of such fuel is burnt, accumulation of these oxides results, offering wayward problems of corrosion and pollution. Total sulfur can be estimated by bomb method (ASTM D 1266 ; IP 107). Maximum permissible amount of sulfur is 0.13% ; in all kerosenes.

2.3.6.7 *Aniline Point*

(IP 2/56 ; IS (1448) P : 3) This test indicates qualitatively the amount of aromatics present in kerosene. This method is fully discussed in diesel fuels.

2.3.7 DIESEL FUELS

Diesel oils are the fractions in the boiling range of 250-320°C ; and fall under gas oil fractions. These are basically divided into two classes as high speed diesels and low speed diesels.

Classification of diesel oils is done according to speed and loads of the engine as given below :

Low speed	Below 300 RPM	For heavy loads at constant speeds.
Medium speed	300-1000 RPM	Fairly heavy loads moderately constant speeds.
High speed	above 1000 RPM	Load and speed vary.

Volatility test for these fuels is of trifle value ; however it is advisable to conduct ASTM distillation test to infer the boiling range. High percentage of light ends (upto 10% distillation) are traits of low flash points. Even though flash point has no direct influence upon performance of fuel, still its minimum value should be maintained to prevent possible fire hazards in handling and storage. If 10%—50% boiling temperature is high, its warm up period will considerably increase. A high boiling point gives much smoke formation and crank case dilution. For all high speed oils 50% point is kept around 300°C ; too low 50% point gives a low viscosity and possibly low heating value too. Table 2.9 gives specifications of high speed diesels.

The general tests recommended for diesel fuels are (in the order of performance).

- (1) Pour point
- (2) Aniline point—Diesel Index (Cetane number)
- (3) Flash point
- (4) Calorific value
- (5) Viscosity

2.3.7.1 *Pour Point*

The criteria of pour point fixation depends upon two factors namely climatic conditions and storage (handling). Fuel, at minimum ambient temperature must be free flowing. In India pour point is fixed at 5°C ; however in the Himalayan belt, where the climate persists at sub-zero level this may not be satisfactory ; hence low pour point oils are essential. It is also observed that at close approach of pour point (within 2 to 3°C), the viscosity increases very much, the result of which is high pumping costs.

TABLE 2.9

SPECIFICATIONS : HIGH SPEED DIESEL OIL

Sl No.	Characteristic	Method	Unit	Requirement
1	Acidity, Inorganic	P : 2	mg KOH/mg	Nil
2	Acidity, Total, Max	P : 2	mg KOH/mg	0.50
3	Ash, Max	P : 4	% wt	0.01
4	Carbon Residue (Ramsbottom), Max	P : 8	% wt	0.20
5	Pour Point, Max	P : 10	°C	6
6	Copper Strip Corrosion for 3 hrs @ 100°C	P : 15		Not worse than No. 1
7	Density @ 15°C	P : 16	g/ml	To be re-reported 45 min
8	Diesel Index	P : 17		
9	Distillation : Final Boiling Point	P : 18	°C	To be re-reported 85/90
	Recovery @ 366°C, Min			33/38*
10	Flash Point, (Abel), Min	P : 20	°C	2.5—7.5
11	Kinematic Viscosity @ 37.8°C	P : 25	cS	
12	Sediment by Extraction, Max	P : 30	% wt	0.05
13	Sulphur, Total, Max	P : 33	% wt	1.1 **/1.0
14	Water Content, Max	P : 40	% vol.	0.05
15	Flame Height, Max	Indian Customs	mm	18

* Subject to agreement between the purchaser and supplier, a lower or higher maximum Flash Point may be accepted.

** Subject to agreement between the purchaser and supplier a lower or higher maximum Sulphur Content may be accepted.

2.3.7.2 Aniline Point

Diesel fuels are mainly composed of paraffins although there is no bar for aromatics. Aromatics of this boiling range present in the fuel cause abnormal ignition delay. For this reason an estimation of aromatics is essential. One such method is aniline point which can predict the suitability of oil. Aniline point is defined as the minimum temperature at which equal volumes

of anhydrous aniline and oil mix together. Diesel index (IP 21/53 ; IS P : 17) a derivative of Aniline point is defined as

$$[0.018 \text{ A.P } ^\circ\text{C} + 0.32] \text{ API.}$$

Aniline being an aromatic compound freely mixes with aromatics ; so a low aniline point indicates, low diesel index (because of high percentage of aromatics). Aniline point can also predict the amount of carbon present in the molecule (aromatics), as given by the formula³⁷.

$$\% C_A = 1039.4 n_D^{20} - 470.4 d_{20} - 0.567 \text{ AP}(^\circ\text{C}) - 1104.42$$

where n_D^{20} . refractive index at 20°C

d_{20} density at 20°C

Diesel index is a measure of ignition quality of fuel. Diesel engine works on the principle of compression ignition. During compression adiabatically the air temperature reaches around 600°C , when the fuel in finely atomised form is fed in, it instantaneously explodes. The temperature at which this explosion takes place without the aid of fire is called self ignition temperature. Self ignition temperature is low for paraffins while it is high for aromatics (benzene 651°C) (See Chapter 2.2). Thus a fuel rich in aromatics burns later causing ignition delay and it gives rise to what is known as diesel knock. For this reason all diesel fuels are processed to have a diesel index in the range of 45 to 55. A high diesel index is also not desirable, as a fuel rich in aromatics gives rise to better calorific value than paraffin rich fuel for equal weights. When the fuel is injected into the chamber of hot air, first the fuel drops acquire the temperature of the surroundings. This takes some time. The time delay can be decreased by atomising the fuel into fine drops and also by varying the composition of fuel. Viscosity also has its own role in heat transmission. Once the droplets acquire the temperature of self ignition, the droplets explode. A continuous flame front may move if the aromatic rich fuel is fed in—obviously a cause for diesel knocking. Fig. 2.20 shows the diesel fuel performance in an engine. During adiabatic compression, the temperature rises and at that instant the fuel is injected. The time taken by the fuel, from injection to explosion is known as delay period. Then the fuel burns at a constant rate. The air pressure and temperature increase after explosion. The two curves A & B

marked in the figure show the characteristic performance of two fuels—'B' is for a fuel rich in paraffins and 'A' is for aromatic rich fuel.

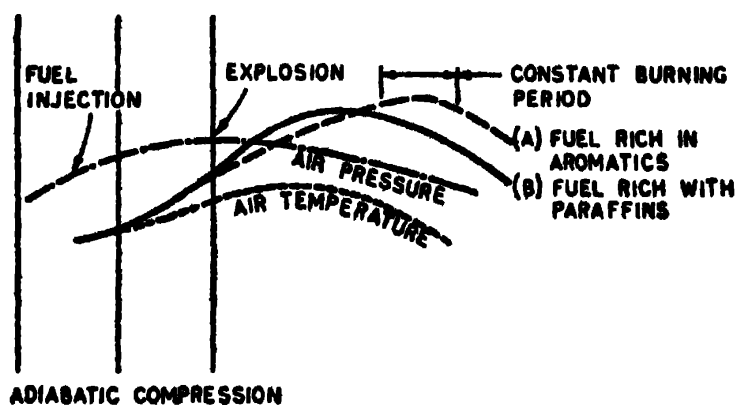


FIG. 220. Diesel oil Combustion Performance in Engine

Peaks *a* and *b* obviously should coincide with crank position, otherwise, knocking results. High speed engines require a fuel of viscosity, 1.4 to 2.5 CS (at 30°C), where as low speed engines may work with even high viscous fuels (5.8–26.4 CS).

Cetane number : (IS P 19 ; ASTM D 613-58T)

Cetane number is a corollary of Diesel index.

It is defined as percentage volume of *n*-cetane in a mixture of *n*-cetane and α -methyl naphthalene, which gives the same ignition delay as the fuel under consideration, when tested in a CFR engine. Some people prefer heptamethyl nonane (Cetane No. 15) in place of α -methyl naphthalene.

A relation between diesel index and cetane number is presented in Table 2.10(a).

TABLE 2.10(a) : Cetane number Vs. Diesel Index.

Cetane No.	Diesel index
30	26
35	34
40	42
45	49
50	56
55	64
60	72

TABLE 2.10(b) : Diesel Fuel Ease of Starting

Ambient Temperature °C	Cetane No.	Viscosity SSU at 37.8°C
-34.4	90	—
-28.9	83	46
-23.3	76	57
-12.2	63	65
- 6.7	56	—
- 1.1	49	—
+ 4.4	43	100
+10.0	36	—

TABLE 2.10(c) : Diesel Fuels—Properties

	<i>High speed</i>	<i>Low speed</i>	<i>Medium speed</i>
Viscosity at 37.8°C			
SSU Minimum	32		32
Maximum	50	250	70
Sulfur %	1.5	2.0	1.5
Conradson Carbon Residue %	0.2	3.0	0.5
Ash %	0.02	0.04	0.02
Water and Sediment % vol.	0.05	0.6	0.1
Flash point °C	—	62.3	62.3
Cetane No.	50	30	40
Diesel Index	45	20	30

2.3.7.3 Flash Point

It has no real significance on performance of fuel. Knowledge of this is required for safe handling and storing. In India flash point of diesel is kept around 50°C—55°C.

2.3.7.4 Calorific Value

Though high calorific value of the oil is desirable, it cannot be at the expense of diesel quality; hence a fuel having^{29b} calorific value 41.83 kJ per gm is sufficient. Apparently paraffins have high calorific value due to higher hydrogen content, but aromatic

tics mainly contribute by bond dissociations. The disparity in calorific value for these materials in this region is not overwhelming.

2.3.7.5 *Viscosity*

Ease of starting depends upon viscosity and ignition quality. At lower starting temperatures high cetane fuels are required (See Table 2.10(b)). Diesels used for different speeds must possess the properties as shown in Table 2.10(c).

Thermal stability of diesel fuels is important, because the remaining fuel from the combustion chamber is returned back to the reservoir. The test is performed by exposing 50 ml sample kept at 149°C for 90 minutes with an additive. When the sample is filtered through a filter paper, the excessive stain on filter paper is an indication of bad oxidation stability of the fuel usually additives like 1-n-butoxy-1-ethane, dioctyl-diphenyl amine (upto 20 ppm, are used to improve the stability of fuel.

2.3.7.6 *Diesel Additives*^{88, 89}

Just like gasoline, diesel fuels are also blended with additives to give satisfactory performance. Ignition accelerators are used for reducing the ignition delay. These are generally oxygen donating substances (oxidising type) like nitrates and nitrites of C₇-C₈ acids (amyl nitrate is an example); aldehydes, ketones, ethers and peroxides. These have the tendency to oxidise the fuel. Inhibitors to stop gum formation are the same type as used in the case of gasoline (phenol amines under the trade name Topanol).

Pour point depressors are generally chlorinated paraffins, and these are used to improve the cold-start performance of the engine. Anti-smoke additives like ethyl lubrizols cause less smoke in the exhausts. Alkaline agents and ashless dispersant additives have been used to improve quality of rail diesels. These alkaline agents provide improved piston ring and cylinder line protection particularly with high sulfur fuels.

Antistatic additives are optional because of the ubiquitous demands of diesel; time of storing is not much, hence these may or may not be mixed. Usually these are the chromic salts of alkylated salicylic acid, calcium aerosols, vinyl methacrylate

polymers. To prevent microbiological growth dioxaborinanes (boron compounds) N-benzylidenemethyl amine are used.

2.3.8 LUBE OILS

The principal source of lubricating oil is the fraction that is left after lighter components, namely gasoline, kerosene, diesel oil during crude distillation. Generally lubes have a boiling point above 350°C and these are obtained as the main products from vacuum distillation units. Residuums, after precipitation of asphaltenes are known as bright stocks and form a good source for lube oils.

2.3.8.1 *Composition of lube oils*

Lubricating oils are composed of paraffins, naphthenes, aromatics and unsaturated bodies. The chief molecular structure of lubes seems to be naphthene rings or naphthenes and aromatic rings arranged in groups of as many as six with paraffinic side chains. The more such chains the more paraffinic the oil is. Naphthenic crudes give more rings with less side chains. Normal paraffins (long chains) in this range are usually waxy in nature and have to be separated for maintaining free flow of oil. Thus a crude oil rich with paraffinic chains gives high viscosity index, less viscosity gravity constant and high stability lube oils. Depending upon the services intended for, lube oils are classified. Nelson²⁹⁰ grouped the oils into seven categories as shown below :

- (1) Machine and Engine Oils (Neutral oils)
- (2) Compounded Oils
- (3) Turbine Oils
- (4) Cold test Oils
- (5) Transformer Oils
- (6) Colour Oils (White Oils)
- (7) Corrosive Oils

2.3.8.2 *Machine oils & engine oils*

These are all high viscosity index oils as they have to serve under varying temperatures. Medium viscosity oils are suitable for most of the industrial applications. Low viscosity index oils

are suitable for compression ignition engines, Aircraft engines require a very high viscosity index oils. These oils are further subdivided into straight, premium, heavy duty, etc. depending upon viscosity index and serviceable temperature. These oils also include spindle oils of (HVI). These are produced from HVI, neutral or bright stocks. Cylinder oils are also HVI grade oils, but at⁴⁰ present our country does not produce them. The availability of bright stock and HVI neutral is at present satisfactory.

Marine grade oils are required to meet critical necessities of performance. Thus, these stocks are produced in our country as blends from indigenous and imported oils. Aviation oils are also special grade oils ; such oils are not produced in India at present. The oils which are used in different services are shown below :

HVI oils for planes, high speed operations

MVI oils for petrol, diesel and stationery vehicles

LVI oils for light equipment.

In fact no single oil is suitable for all types of applications. This has called for blends of multigrade oils. All multigrade oils contain viscosity improvers. As an example, a multi grade blend of SAE 30 and 10W, can have the starting viscosity corresponding to that of SAE.10W, while in operation it can show the characteristics of SAE 30. The trend of viscosity variation of such blend is shown in Fig. 2.21.

2.3.8.3 *Compounded oils*

These are lube oils fixed with animal or vegetable oils. These oils exhibit more wettability characteristics which makes them suitable for steam engines, compressors and quenching and tempering operations. Emulsibility is considered to be more important than viscosity index of these oils.

2.3.8.4 *Turbine oils*

High speed machinery, such as steam turbines, electric motors should have emulsion-free oils. Extreme stability is required for such oils.

2.3.8.5 Cold test oils

These oils are mainly used in refrigeration and hydraulic systems, specially designed for arctic climates. Pour point is the major important thing compared to all other properties of oil.

2.3.8.6 Colour oils

These are industrial oils used in textiles, food and paper industries. Medicinal oils must be very thoroughly freed from colours and must have high stability. Depending upon the application, the concentrations of sulfur, aromatics and resin bodies are fixed.

2.3.8.7 Corrosive oils

Some oils are blended with corrosive ingredients. These are used in cutting, shaping of metals. Heavy duty oils and extreme pressure lubes are of this category.

Above classification by service is no doubt suitable for almost all applications. Physical properties are to be included for a technical classification. Accordingly SAE classification and Bureau of Ships classification have come into service, which set forth the physical parameters for application.

SAE Classification for Crank case oils¹²

(Viscosity in c.s.)

S A E No.	Viscosity range				
	at -18°C		at $+99^{\circ}\text{C}$		
	Min	Max	Min	Max	
5 W		1,300			
10 W	1,300	2,600			
20 W	2,600	10,500			
20	—	—	5.7	< 9.6	
30	—	—	9.6	< 12.9	
40	—	—	12.9	< 16.8	
50	—	—	16.8	< 22.7	

As lube oils are made for a wide variety of applications it is not possible to make a single product to meet all the require-

ments. As a consequence lubes are formulated for a particular application, hence large formulations are indubitable.

Whatever may be the special formulation, all lubes are to be submitted to tests, as given below : (Special tests are not mentioned here) :

- | | |
|-----------------|-----------------------------------|
| (a) Flash point | (c) Viscosity and Viscosity index |
| (b) Pour point | (d) Oxidation stability |
| | (e) Carbon residue |

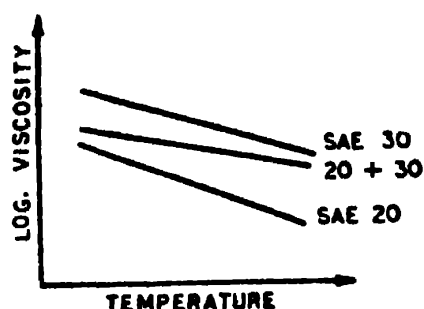


FIG. 221. Viscosity Variation of multigrade oils with Temperature

2.3.8.8 Carbon Residue

The propensity of cracking is indicated by carbon residue of the oil. Heavy oils being delicate to high temperatures, have a tendency to crack, with deposition of carbon. Lube oils are often subjected to such hazardous temperatures. The amount of carbon formed during cracking does ultimately provide an idea of usability of oil at high temperatures. This test is conducted by two methods namely Conradson method (IP13/66) and Ramsbottom method (IP 14/65 ; IS : 1448 P : 8).

2.3.8.9 Conradson method

A sample of 10 gms is taken into a silica-crucible and heated out of contact with air. The set-up provides the necessary precautions, such that the oil is thermally decomposed out of contact with air. The decomposition is brought by means of high heating rates. As the heating continues fumes appear at the chimney top. The fumes are burned and heating rate is adjusted

such that the burning sustains, but the flame is never allowed to cross the bridge of the chimney. (See Fig. 2.22). After the

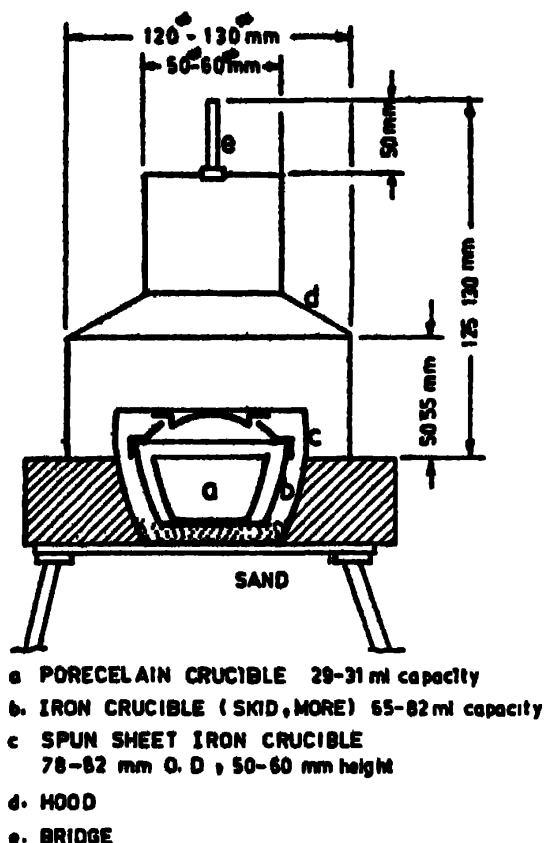


FIG. 2.22. Conradson Carbon Residue Apparatus

burning of the fumes further heating is continued. Afterwards, the set is cooled and the silica crucible is weighed to get the weight of carbon deposited. Expressed in percentage gives Conradson carbon residue.

Prescribed heating rates :

Initial heating (Fumes appear and capable to burn continuously, when ignited)

Pre-ignition period 10 ± 1.5 min.

Burning of fumes (Burning of fumes without crossing the bridge of chimney.

13 ± 1 min

Strong heating (For complete decomposition of oil)

7 min

Total time 30 ± 2 min.

If the above schedule is unable to be followed, the burning period of fumes should only be taken into account. Very high rates of heating are required to keep up the schedule.

2.3.8.10 *Ramsbottom method (Fig. 2.23)*

In this method the sample is carefully fed into a glass bulb which has a capillary end. The bulb is kept into a heating bath kept at 550°C. The sample is allowed to decompose for 20 minutes. After heating is over the bulb is cooled and weighed to find the carbon formed. Amount of material to be taken is inversely proportional to coking tendency of the oil.

Expected Carbon residue	Size of sample for experimentation
2%	4.0 gms
2—4%	2.0 gms
4%	1.0 gms

Best quality of oils give less carbon residue under serviceable conditions. Conradson carbon residue of this should not exceed 0.2 to 1.0%. Paraffin oils give less carbon residue compared to naphthenic oils.

2.3.8.11 *Oxidation stability*

This test reveals the deterioration characteristics of oil on oxidation. Oils are generally in contact with air and hot surfaces, thus oxidation is inescapable. Higher paraffins are easily oxidised compared to naphthenes and aromatics. Major amount of lube oil is paraffin, which is more prone to oxidation. In the laboratory the test is conducted (IP—48/62) by passing air at a rate of 15 litres per hour through a sample of 40 ml kept at 200°C for 6 hrs. Second oxidation period for another 6 hrs. at the identical conditions for the same sample is carried out. After oxidation periods are over, the sample is cooled and its viscosity and carbon residue are found out and compared with the original sample. Papers on the chemistry of oxidation of fuels and its inhibition have been authored by Bettoney et al⁴⁴ and Lod Wick.⁴⁵

All oils of high boiling points are susceptible to this natural oxidation which proceeds by free radical mechanism. So, inhibitors prevent the free radical chain propagation and increases

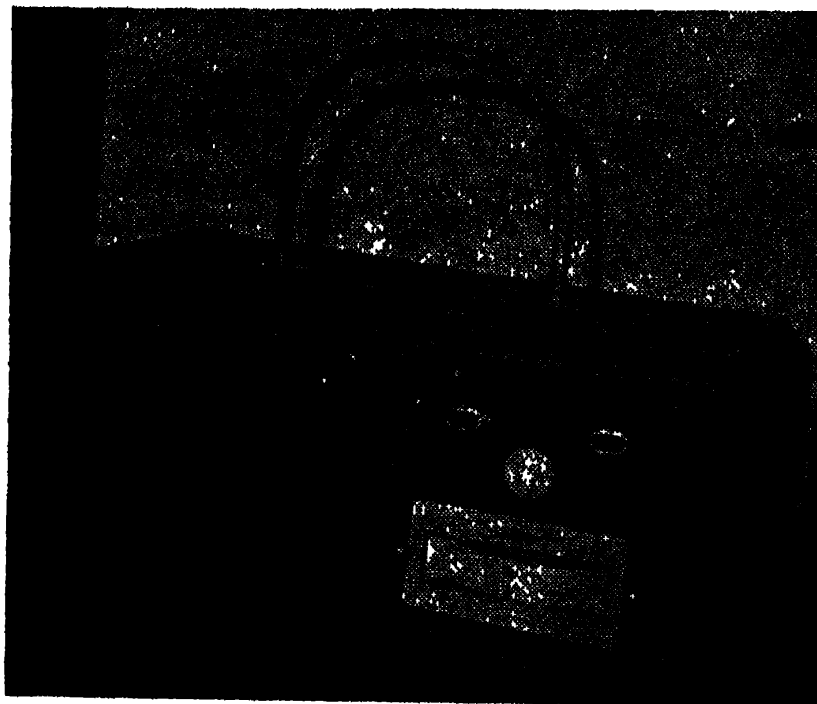


FIG. 2.23 Ramsbottom apparatus

the resistance of oil to oxidation. All oils in general are blended with such additives.

Additives and their functions in lube oils are presented in Table 2.11. Additives supplied by different companies also accompany in Table 2.12.

2.3.9 TRANSFORMER OILS

These oils are used in electrical industry mainly for insulating, cooling purposes; additionally these oils protect the equipment from moisture compared to vegetable or coal distillate oils, petroleum oils are found to be more suitable because of high viscosity, thermal stability & hydrophobic nature. Petroleum oils used in electrical industry fall into two categories^{41a}; Oils in transformers & circuit breakers etc. belong to one class; other class of oils are generally used for impregnating cables & papers used in electrical industry. Oils used in transformers are low

viscous, thermally stable but having high boiling points, in close ranges. Second type oils are highly viscous and act as insulators only. The deterioration of these oils in service is closely connected with the oxidation characteristics of oils. Oxidation products are mainly acids which cause sludge formations.

Important tests for transformer oils

- (1) Acid value (ASTM D 974)
- (2) Dielectric strength
- (3) Flash point
- (4) Pour point
- (5) Sludge value
- (6) Copper corrosion test

2.3.9.1 *Dielectric Strength*

High dielectric strength is required for oils employed for insulation purpose. Even though high electric strength does not give any indication of degree of refinement of oil or oil contaminants, it ensures the freedom of oil from water and other adventitious matter. Electric strength or break down test is performed by increasing the voltage at a rate of 2 KV/sec in between electrodes of 12.5 to 13.0 mm dia. which are placed at a distance of 2.5 ± 0.1 mm. The cell capacity is usually between 300 to 500 ml. The voltage is continuously raised until break down takes place. A satisfactory oil test (IP 20/73) should show a break down strength of around 120 KV/cm.

2.3.9.2 *Permittivity* (dielectric constant)

It is the ratio of capacity of a capacitor in which oil is dielectric; to the capacity of air when this acts as dielectric. The range of permittivity should lie between 2.1 to 2.3.

2.3.9.3 *Sludge Value*

Oils contain some products which give rise to sludge formation. Sludge value is found out by precipitating insolubles with heptane. This test is performed before oxidation of the oil and after oxidation of the oil. High sludge formations indicate the negative quality of oil, which also indicates the high percentage of oxidative products.

TABLE—211
ADDITIVES FOR LUBE OILS

<i>Purpose</i>	<i>Additive</i>	<i>Quantity</i>	<i>Ref :</i>
Pour point depressors (depress the pour point of lubes and other fractions for crude Laudding)	Poly alkyl metha ^a crylates ^b Maleic-fumaric esters Curene ^c	(0—1%) gives 5°C depression (0.1%) gives 10°C 0.2—0.5% for 9°C	a. J. K. Rostogi, 2 LAWASP IIT. Bombay b & c ; M. C. Dwivedi & R. Vipradas, 2 LAWASP d. N. K. Purohit 1st LAWASP, Nov. 22-23 ; 1978 IIT. Bombay. e. C. C. Colyer, 7 WPC, 1967, Vol. IV, P 294 f. H. M. Noel Pet. Ref. Manual Reinhold, P 147
Oxidation inhibitors (prevents oxidation of unsaturates)	Chloro paraffins Wax-naphthalene phenol condensates	0.1%—5°C	
Corrosion inhibitors (to prevent chemical attack on metal surfaces)	Phenols ; chloro acetoni- trites Amines Higher organic acids alkyl ammonium acid phosphates (Benzyl phosphates)	0.4—2%	
Anti-bearing corrosives	Hydrazides, zinc dialkyl dithiophosphate sulfuris- ed terpens	0.5%	

TABLE—2.11 (Contd.)

Purpose	Additive	Quantity	Ref :
Antiwear improvers (For protection of surfaces of high friction by forming protective films)	Fatty acids, dibenzyl disulfide, Tricresyl phosphates*		
Detergents (Clean surface exposures and eliminate deposits) keep oil insoluble material in suspension.	Organometallic compounds, Soaps of Ca, Mg, Ba, etc. Poly amines or sulfonates	2 to 10%	
Dispersants (to keep sludges in suspension and not allowing them to deposit)	Organometallic compounds of Ca, Sr.		
Anti foams	Silicones	f 0 001%	
Rust preventors (prevents rusting even in presence of moisture)	Soaps of fatty acids ; Metal sulfonates		
Viscosity index improvers (improve viscosity temperature relations)	Poly olefins, ^d Styrene polymers Acrylate polymers		

TABLE-2.11 (Contd.)

Purpose	Additive	Quantity	Ref :
Oiliness (to improve thin film characteristics)	Vegetable and animal oils		
Extreme pressure agents (when heavy loads, and shock loads are encountered)	Esters of fatty acids, sulfonic acids ; sulfurised molybdenum esters Penta erithritol oleates and Bisphosphoramides, dichloro, dibenzyl disulfide lead naphthenates.		
Water repellants (Settle water from oil phases)	Long chain fatty acids, silicones ; boron compounds or hydrophobic polymers	200-2000 PPM	
Emulsifiers (when emulsions are required).	Sulfonates, naphthenic acids, mono alkyl amino borates, Lithium soaps.		

TABLE—2.12
ADDITIVES SUPPLIED BY DIFFERENT COMPANIES

Gasoline anti-oxidants :		Chemical	Quantity	
Ethyl Corporation	701	2, 6, di, tert, butyl phenol	1-4 Kgs/1000 Barrel	
Dupont	AO-5	<i>n-n</i> butyl-p-amino phenol	1-5	-do-
Lubrizol	803	2, 6 di-t-butyl p-cresol	2.5 to 10	-do-
Amoco	533	2, 6 di-t-butyl p-cresol	2.5 to 15	-do-
UOP	No. 85	dioctyl-p-phenylene diamine		
<i>Metal deactivators</i>				
Dupont	D M D	N, N' disalicylidene 1, 2 diamine propane	0.1 to 1.5	-do-
Lubrizol		-do-	0.4 to 1.2	-do-
Ethyl Corporation	M D A	-do-	0.2	-do-
<i>Corrosion inhibitor</i>				
Dupont	AFA-1	alkyl amino		
Petrolite Corporation	KONTROL-157	alkyl phosphate Not known	0.5 to 10 —	-do-
<i>Ignition Controls</i>				
Amoco	541	Phosphorus Compounds	0.2-0.4 T	
Ethyl Corporation	KC-1	Bis-thiono phosphate	0.2 T	
	ICC-4	Tery methyl phosphate	0.2 T	
Monsanto	CDP	Gresyl diphenyl phosphate	0.2 T	
(T : theoretical requirement to convert lead in gasoline to Pb ₃ (PO ₄) ₂)				
<i>Detergents :</i>				
Amoco	572		2.5 to 12.5 Kgs/1000 B	
Lubrizol	580		1.75	-do-
Anticings	Dupont	DMF	Vol. % .02 to 0.1	

TABLE—2 12 (*Contd.*)

	Chemical	Quantity
<i>Multifunctionals</i>		
Dupont	Amine salts of alkyl	2.5 to 10 Kgs/1000 B
DMA-4	phosphates	
DMA-5	DMA-4 plus cresyl	5 to 45 -do-
	diphenyl	
	phosphate	
<i>Biocides</i>		
Phillips		200-1000 PPM
PFA 55 MB	Biobar JF	135-270 PPM
Sohio		

2.3.9.4. Copper Corrosion Test

The use of copper in electrical industry is immense, hence the attitude of oil towards copper should not be calamitous. Satisfactoriness of oil can be verified by heating a copper strip in oil for 3 hours at 100°C and observing the copper strip. Discoloration of the strip is direct indication of corrosiveness of the oil as given below :

Appearance of Sample (Copper strip)

Light Orange, looks like a fresh one	— (1)
Dark Orange to red or multi coloured	-- (2)
Multi coloured with greenish tinge	— (3)
Dark grey to black colour	— (4)

International Electro Technical Commission (IEC) test involves the blowing of air through oil at 150°C for 45 hours in presence of copper strip. After oxidation, the oil is tested for acidity and sludge.

Indian specifications of transformer oil is given below :

1. Sludge value (Heptane by wt)	1.2% Max
2. Acidity mg KOH/gm after oxidation for 164 hrs at 100°C	0.4 K(OH)/gm (fresh) 2.5 Max
3. Electric strength one min.	40 K.V.
4. Saponification value mg KOH per gm in oil	1.0 Max
5. Acidity gm KOH/gms of oil	0.03
6. Viscosity at 27°C CS	27 Max
7. Pour point °C	—10 Max
8. Flash point °C (Pensky Martin Apparatus)	140 minimum
9. Copper strip corrosion (at 100°C for 3 hrs)	Not more than 1
10. Resistivity at 90°C ohms cms at 27°C	13×10 ¹² min 500×10 ¹²
11. Specific Gravity	0.89 max

2.3.10 BITUMEN

Bitumen is the residual product obtained from crude distillation unit. It is essentially solid at room temperature and has got very high viscosity. Asphalt is usually a mixture of bitumen in oil, containing much mineral matter. Bitumen natural deposits are also available; famous Trinidad pitch lake is such a deposit. Bitumen obtained from the distillation column is poor in qualities. This has necessitated air blowing of bitumen to obtain suitable grades. Most of the bitumen is used in high-way constructions, waterproofing and coatings works.

Bitumen is specified by the following two tests

- (a) Softening Point
- (b) Penetration index.

These two tests do not describe the properties of bitumen completely. Other tests like viscosity, volatility, durability, ductility are necessary for obvious reasons. Outlines of these tests and significance are mentioned below :

2.3.10.1 *Softening Point (ASTMD 1398 IP.198 Ball & Ring test)*

Bitumen being amorphous does not melt sharply. The softening point is found out by the Ball & Ring Test. Bitumen is first melted and casted into discs of two numbers in standard rings. A steel ball weighing (3.5 ± 0.05) gms (dia 9.53 mm) is kept on each casted disc of bitumen. The whole stand carrying these two discs with balls is immersed in a water or glycol bath. As the heating proceeds, softening occurs. The temperature at which the sample detaches from the die and falls; indicates its softening point. The two samples from such rings are supposed to fall within a difference of 5 seconds. Higher the softening point, the better is consistency of bitumen. (See Fig. 2.24).

2.3.10.2 *Penetration Index*

The hardness or penetration quality of bitumen is assessed by this test (IP 49/72).

A standard needle is allowed to penetrate under a load of

100 gms, through a sample kept at 25°C for 5 sec. Distance travelled under those conditions indicates the consistency of

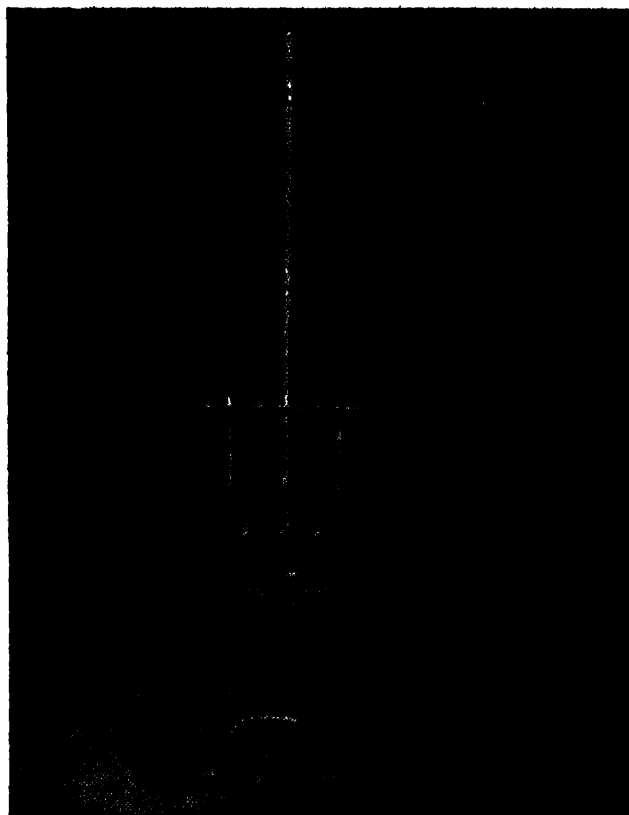


FIG. 224. Smoke point apparatus

sample. The distance (easily) travelled would naturally depend upon its load, and softening point. More penetration index naturally impairs the surface applications, where hardness is sole criteria.

2.3.10.3 Ductility (D 113)

Bitumen must possess good ductility, when it is used in surface application. The ductility is measured by a ductilometer. Ductility is a measure of the capacity of bitumen to elongate or stretch. This test is carried out by pulling a test piece of bitumen of standard dimensions at a uniform rate (5 cm/min) keeping sample at 25°C. Higher capacity for elongation indicates that the sample is having a high ductility.

Other tests like viscosity, boiling point, ash content are

desirable. Suitable solvents are added to solubilise the bitumen and then applied over the surface, when the solvent evaporates a fine layer of bitumen appears. These type of bitumens are called cutback bitumens. These cutback bitumens, after full curing period must possess the same properties as the bitumen from which they are made.

Indian specifications of bitumen are given below :

BITUMEN
IS SPECIFICATIONS

Grade	Sp. Gr. 27°C	Flash point °C min.	Soft point °C	Penetration	Ductility cm min	Solubility in CS ₂ % max
75/15	1.0 —1.05	200	65—80	10—20	25	99
65/25	"	"	55—70	20—30	10	99
75/30	"	"	70—80	25—30	3	99
85/25	"	"	80—90	20—30	3	99
85/40	"	"	"	35—45	3	99
90/15	1.0 —1.06	"	85—100	10—20	2	99
105/20	"	"	95—115	15—25	2	99
115/15	1.02—1.06	"	110—120	8—20	2	99
135/10	1.02—1.07	"	130—140	7—12	1	99
155/6	1.02—1.07	"	150—160	2—12	0	—

Grade 75/15 means softening point 75°C and penetration index is 15.

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PROBLEMS

1. Draw the ASTM distillation plots of marketted gasoline and kerosene. Convert these plots into EFV lines at atmospheric pressure and see whether there is any continuity, if not find the overlap.

2. (a) From the given data, draw TBP graph and asses the qualities of different fractions.

(b) Convert TBP curve to E F V curve for the above crude at 150 kg/cm².

Java, Indonesian crude

API : 28.8

P.Pt : 41°C

Sulfur wt : 0.11%

Vis. cs.

60°C : 56.1

45°C : 128.1

Sal Kg/1000 bbl : 70

Wax. wt% 23.8

C.R. 8.1%

Light naphtha

C₈-100°C : 2.6% by vol.

Sp. grv. 0.701

Paraffins%	62
Naphthenes%	30
Aromatics%	8
RON	70

Naphtha

100–155°C	3.0% by vol.
sp. gr.	0.755
Paraffins%	46
Naphthenes%	43
Aromatics%	11

Kerosine

155–295°C :	13.4% by vol.
Sp. gr.	0.813
Aromatics vol. %	15.5
Sulfur wt.	0.04%
Smoke point	19

Heavy distillate

295–350°C	7.3% by vol.
Sp. gr.	0.834
P. Pt.	15.6°C
Diesel index	72
Catane no.	66
Sulfur wt. %	0.08
Viscosity(CS) at (38°C)	– 5.53

Residual oil

More than	350°C · 72.9% by vol
Sp. gr.	0.915
P. Pt.	58°C
Sulfur wt. %	0.12
Vanadium Nickel Iron PPM	1.6/0.6/24
Viscosity at 80°C	280 (cst)

3. (a) Estimate the gross calorific value of a kerosene fraction having an API gravity of 48 from eq. 2.13.

(b) Estimate the heat energy required in raising the temperature from 35°C to 82°C. The fraction has a cubic arrange boiling point 204.5°C. (use eq. 2.11 and Fig. 2.6(a))

(c) If this fraction were to vaporise completely, find the specific heat of fraction in vapour phase (use eq. 2.12).

4. A natural gas having a calorific value of 43.4 MJ/M³ and density of 0.632(gms/lit) is allowed to burn at 5 milli bars ; a replacement with another gas of 25 Wobbe number is sought. Find the pressure at which the gas should be combusted ?

5. 3000 kilo liters of gasoline of 74 API has to be stored in a tank of suitable capacity under varying temperatures of a maximum fluctuation 22°C. Assuming an average temperature of 25°C design a suitable storage tank. Find the breathing losses.

6. (a) 150 Neutral oil, is having a viscosity of

$$\frac{134 \text{ SSU/at } 38^{\circ}\text{C}}{(28.8 \text{ cs/})} \text{ and } 42.4 \text{ SSU at } 99^{\circ}\text{C}$$

Find the viscosity index (consult 1P tables for getting standard value of L & H).

(b) From its VGC value classify the nature of oil (API gravity 30).

7. Estimate the viscosities of toluene and ethylbenzene, by Souder's method at 25°C.

8. Find the vapour pressure of a chlorinated methane at 120°C using Claussius—Clapeyron equation.

B.P. 76°C.

Latent heat of vaporisation at boiling point : 7140 Cals per gm mole
(Ans : 1440 mm Hg)

9. Vapour pressure of a hydrocarbon is represented by the following eqn. $\log P(\text{atm}) = \frac{-314.49}{T^{\circ}\text{K}} + 8.05$

Calculate the latent heat at one atmospheric pressure and boiling point 165°K (neglect liquid volume).

(Ans. 1200 Cals/g.mole)

10. The thermodynamic properties of a paraffin gave the following values at 32°C and 3 Kg/cm².

Density of liquid = 0.5635 gm/cc.

Density of saturated vapour = 0.00756 gm/cc.

Latent heat of vaporisation = 85.2 gm cals/gm.

The vapour pressure as a function of temperature was found to be represented by the equation

$$\log P(\text{atm}) = a + \frac{b}{T} + 1.75 \log T + CT$$

where $T = ^\circ\text{K}$

$$a = 1.756$$

$$b = -1337.8$$

$$c = 0.004$$

with the aid of Clapeyron equation test the consistency of the above relation.

11. Explain how ATF differs from aviation gasoline. What are the additives required for a good ATF ?

12. (a) What are the different additives used in gasoline and diesel oils ?

(b) Explain the effects of paraffin rich fuel in spark ignition engine.

CHAPTER 3

Fractionation of Petroleum

3.1 Dehydration and Desalting of Crudes

All crudes contain moisture and salts to varying degrees. Water is likely to occur in emulsion form when the crudes are naphthenic or sulfurous. No harm may be expected to the distillation column due to the presence of moisture, as there is always steam in distillation. However, crude has to be dehydrated to remove the salts. Water being good solvent for these salts, the removal is very much effective in the form of brine. Of all the existing salts, chlorides of calcium and magnesium distinguish themselves in playing an invincible role in overhead corrosion. These salts in presence of steam at 150°-200°C easily hydrolyse generating hydrochloric vapours. These vapours cause corrosion to the equipment. Any crude that contains¹ more than 5 kgs of total salts expressed in terms of sodium chloride per thousand barrels may be regarded as salty crude.

Long standing of crudes may permit the separation of aqua phase along with salts and other suspended impurities (brought during mining operations) ; in other words dehydration removes all salts. In general, dehydration of crude is practised in two stages ; first at the site of mine and later in the refinery.

The following general methods are versatile for dehydration of crudes.

1. Chemical treatment
2. Gravity settling
3. Centrifugal separation
4. Electric desalter

At the oil field, salt is removed by settling or by adding chemicals or by combination of these two. Crudes possessing

emulsifying characteristics are not responsive to the settling method; these demand demulsifying agents to increase the coalescence of water drops. Soda ash (0.5 to 5%)^{3,5}, sodium hydroxide; salts of fatty acids (0.05 to 4%), petroleum sulfonates are such chemicals; which hasten the agglomeration of water droplets. A good amount of water should be available in crude for such treatment; lack of water demands fresh additions to the extent of 20% even. After adding the chemicals and water to the desired extent the crude mixture is allowed to stand at 75-80°C, at a pressure of 15 Kgs/cm² in huge tall tanks. Pressure ensures the retention of volatiles in the crude. Demulsifying chemicals, if necessary are added in very small amounts i.e. few hundred ppm. The storage capacity of such tanks is stupendous and reaches up to 3000 Kilolitres. Good separation into hydrocarbon and aqueous phases results when the crude is allowed to stand for 48 hours. (See Fig. 3.1a). ,

Coalescence is also aided by passing the mixture through towers packed with gravel. The settling techniques are not effective and time consuming. Continuous operations are not possible with the result large amount of space and equipment are to be isolated for this purpose. Similarly centrifugal separation is also not economical due to the huge energy requirements and less quantity handled; all these have given the way to electric desalting.

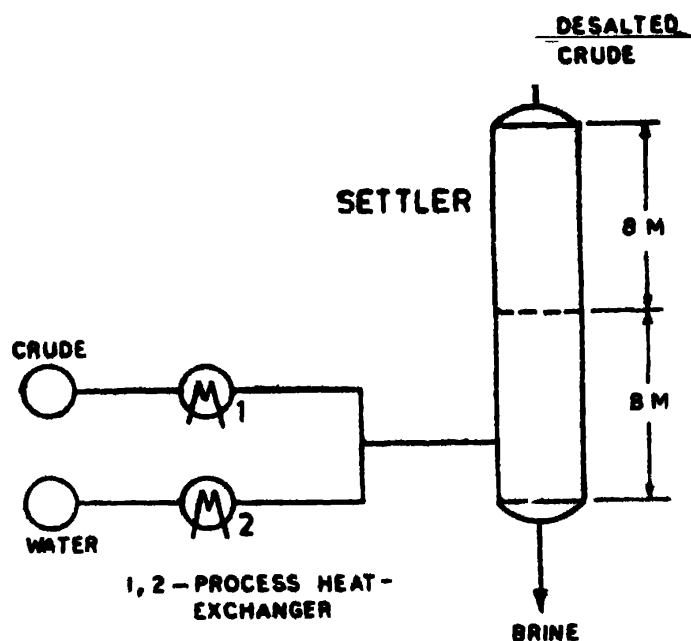
3.1.1 ELECTRIC DESALTING⁴

Simultaneous desalting and dehydration is achieved in this unit with a spectacular removal of more than 90% salt in just less than half an hour. The principle in this separation is very simple; under a charged electric field the polar molecules orient. A potential of 20,000 to 30,000 volts is applied between electrodes through which crude is passed. Water present in the form of emulsion also coalesces and agglomerates into a stream entrapping all the salts in this process. Brine collects at the bottom of the desalter, while crude floats above and forms a separate stream.

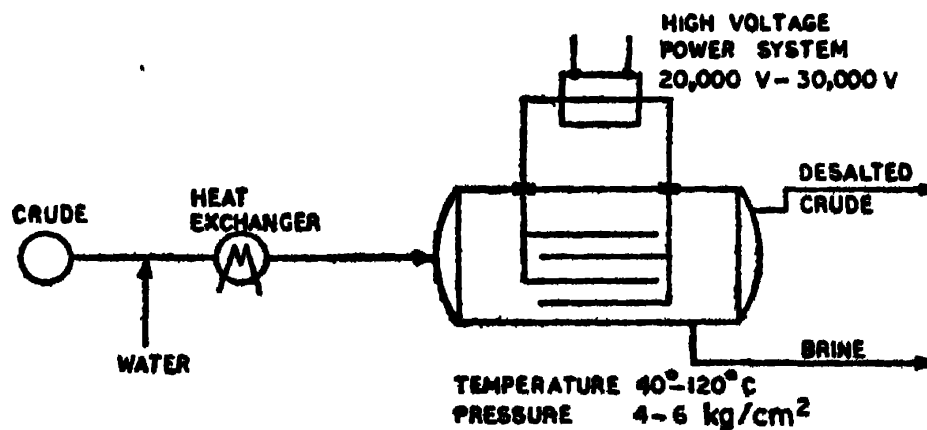
Compactness, efficiency and ease of operation of these units are indubitable and induced every refinery to adopt. Temperature during electric desalting is maintained around 90°C and a

pressure of 5 to 6 Kg/cm² is also superimposed. Power consumption is also very small, frequently of the order 0.01 Kwhr per barrel.

Electric desalting technique is purposefully employed in treatment of distillate stocks, although the aim is different. Acid or caustic treated stocks are liable to form emulsions. These emulsions are efficiently broken by electrostatic field. Catalyst poisoning salts can also be favourably removed. Thus it can form



(a) Settling method



(b) Electric method

FIG. 3.1 (a) Desalting by Settling Method.
(b) Desalting by Electric Method.

an alternative method for pretreatment of catalytic cracker feed stocks.

Fig. 3.1b shows electric desalting technique and Table 3.1 furnishes the information regarding various crude treatment techniques.

TABLE 3.1

Treatment of crudes⁵ :

	Temperature °C	Type of treatment
Chemical separation	60-90	0.05 to 4% sol. of soaps in water +0.5-5% soda ash
Electrical	60-90°C	20,000 Volts
Gravity	80-90°C	Water added upto 4%
Centrifugal	90°C	20% water added

3.1.2 PUMPING OF WAXY CRUDES

An important factor that stands in the way of pumping crude is its pour point. Pour point is directly related to the wax content of oil. Indian crudes are waxy and hence have relatively high pour points. Middle east crudes which are credited with high sulfur exhibit astoundingly low pour points. Crudes from Assam are characteristically famous for high pour points; (wax content 16%, pour point about 30°C). Although it is not essential that all crudes from the region should display the same qualities, in fact often differences exist in the crudes obtained from the same field (different wells). To pump such crudes, is extremely difficult. Often the temperature of the environment falls much below the pour point. It is seen that viscosity near the pour point abruptly shoots up, adding to the difficulties in pumping. Such crudes can be transported only after conditioning. At the oil field of Nahorkatiya such conditioning plant exists. This plant is only one of its kind in the world.

The principle behind the conditioning is based upon the behaviour of wax itself. Crude oils containing high wax often respond to specific type of heating and cooling. At a definite rate of heating and cooling, the response to retain the mobile and pumpable characteristics of crude are illustrative and taken advantage of. These characteristics once attained shall last till further drastic conditions of heating are administered. The conditioning of crude starts with cycles of heating and cooling. Firstly, heating is done up to 95°C , followed by cooling^{6,7} in two stages. First cooling goes down to 65°C followed closely by another cooling cycle to 18°C at a rate of 0.5°C per minute. This way, the planned operation successfully modifies the crystal structure of wax to permit the flow. Two such plants are planned by Oil India Limited at Duliajan and Moran.

Other treatments that can be given to waxy crudes are :

- (a) Diluent addition
- (b) Chemical additives

3.1.2.1 *Diluent addition*

Solvents although they can be employed for this purpose, are not used due to the very nature of contamination of the products. Best diluent can be water, but required in huge amounts, needing large pumps and pipe lines. Economic feasibility may be ascertained before such thing is attempted.

Chemical additives : Cheap chemical additives which can depress the pour points, if available economically, then the treatment shall be capturing and becomes an irreplaceable one in industry. This can obviously remove the ills of conditioning plants where huge amounts of energy and time are lost. These additives⁸ are also known as flow improvers. These additives act by changing the structure of wax and retard the crystal growth. Obviously modification of wax structure reduces viscosity. Even small quantities of additives. (say 300-800 ppm) can markedly depress the pour point by 10 to 16°C . Usually these additives will be incorporated after preliminary desalting operations at the mine. After stabilisation which lasts for a period of 40 to 60 hrs, the crude will be ready for transportation to refinery. The stabilised crude will be in a position to retain the influence of additives at least for a month's time during which refining may be done to completion. The additives being hydrocarbons in

nature, heating crude to distillation temperature can easily decompose them.

A note on Indian crudes at this juncture is worthy. Crudes of India being waxy, naturally drain a substantial amount of foreign exchange in getting the flow improvers. This has become imperative on the part of Government to go for native additives. Accordingly indigenous additives like 'Flowcell' developed by Excel Industries and SWAT 104, 105 & 106 developed by Regional Research Laboratory, Jorhat, play a vital role in transportation of Eastern and Bombay High Crudes in the near future. These additives, it seems remarkably lower the pour points by 10 to 15°C at a marvelously low concentrations of 300 ppm. Also simultaneous reduction in viscosity down to 7 to 12 cps helps in easing the pumping characteristics.

3.2 Heating of crude

Pipe Still Heaters

Refinery processing is basically a fact rested upon effective distillation and condensation. Before the introduction of pipe still heaters (1918) into refinery operations, the direct heating stills (convective type) were used for all heating operations. Non-uniform heating and excessive heating could not be abated satisfactorily in these stills; with these inescapable difficulties, the refinery could not be magnified or utilised for high capacities at short notice, thus, one has to be content with small refinery sizes. The introduction of pipe still heaters, and other chemical engineering appliances into refinery, has tremendously increased the activities in trade. Modern refineries are thus compact in size and accurate in control, with a degree of flexibility in operations for quality and quantity production; hence at short notice the production pattern can be changed without much change in economy. The versatile use of pipe stills from topping of crude to cracking techniques is exciting.

Pipe still heaters are different from old still heaters in one way; the radiant section is separated from convection section. Prudent planning of radiant and convection sections are primary considerations for a pipe still heater for efficacious operations. The recent developments in pipe still heaters have brought the

heat transfer in radiant section as high as 70%. The stack losses and heater losses are brought down to 12% and 5% respectively followed by a close response to control.

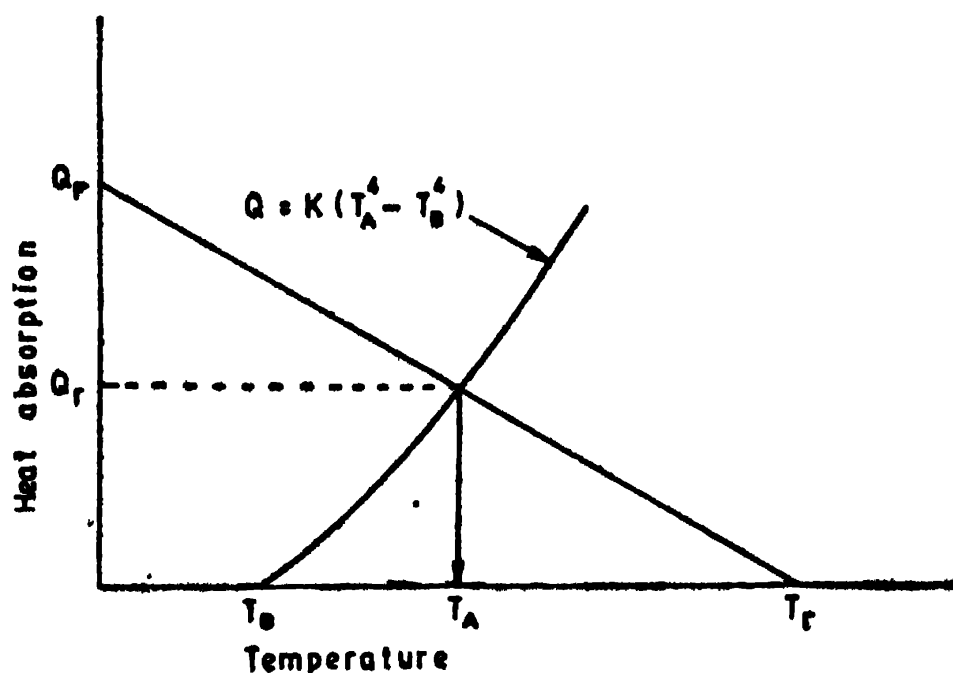
Pipe heaters can be conveniently categorised into three types :

(1) Box/Rectangular, (2) Cylindrical and (3) Radiant Wall.

All these furnaces have got separate radiation section and convection section. The most universal classification is based on direction of tubes as well as shape of furnace and mode of application of heat.

3.2.1 ABOUT RADIATION

In most of the furnaces, the direction of tubes is horizontal as in all box type heaters and vertical in cylindrical stills. Radiant walls also use horizontal tubes, however tubes can be placed



Q_r = Rate of heat release

Q_a = Rate of heat absorption

T_A = Temperature of combustion space

T_0 = Temperature of receiving body

T = Pseudo flame temperature

FIG. 3.2 Locus of heat absorption (Stefan Boltzman Equation)

vertically also. The radiant section design is based upon Stefan-Boltzman equation given as :

$$Q_r = 4.88 \times 10^{-8} [T_G^4 - T_B^4] \quad (3.1)$$

Where T_G and T_B are temperatures of furnace and tube in $^{\circ}\text{K}$. Q_r radiant heat transfer (K. cal) per unit area (Sq. meter) and time (hr).

The equation is graphically represented in Fig. 3.2. The locus of Q_r is shown to be the point of intersection of tube skin temperature and temperature of combustion space, which incidentally relates the pseudo flame temperature (T_r).

This equation enables one to judge the amount of heat transfer as proportional to the difference of fourth power of temperature of the heat generating body and the receiving body. This differs very much from convection and conduction, where heat transfer is proportional to gradient only i.e. the temperature difference of the operating levels. However, here the properties of material receiving the radiation are also important. The properties are not like conductivity or heat transfer coefficient, as intended in other heat transfers, but the visible colour of the material only. As black body absorbs all the radiation that falls on it, its emissivity is expressed as unity and other bodies (coloured) graded accordingly. Except mono atomic gases, all other gases and vapors aid this mechanism. The angle of vision or in other words, the surface which can directly see the flame is also very much important.

3.2.2 CONSIDERATIONS FOR DESIGNING RADIANT¹⁰ SECTION

(1) *Heat duty*

Different heat transfer rates are necessary for different types of operations as shown in Table 3.2. Heating rates are specified either on the basis of projected area of tube or outside surface area of tube. Care should be exercised not to exceed the heat density either on surface of the tube or in furnace.

(2) *Air fuel ratio*

Fuel in radiant section does another duty above the normal heating duty, i.e. it assists radiant heat transfer owing to the presence of tri or multi molecular gases. Consequently a fuel

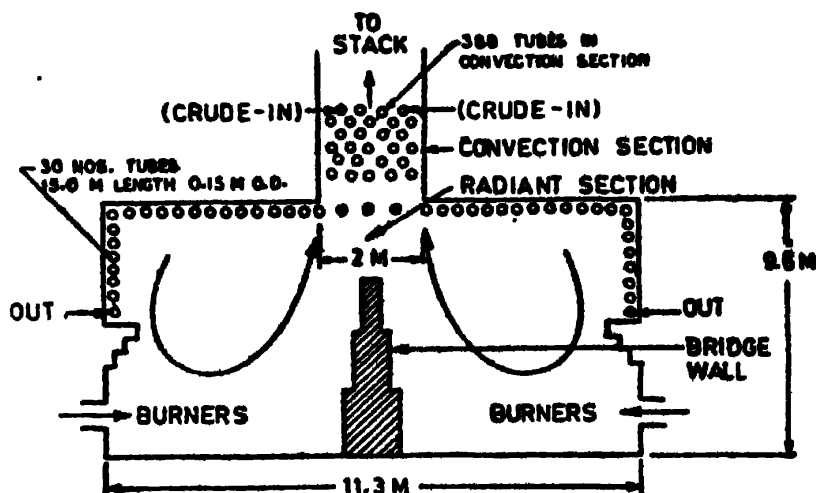
rich in hydrogen gives better radiant heat transfer due to the formation of water vapour after combustion. The ratio of water vapor to carbon dioxide usually depends upon the air fuel ratio. Excess of air fuel ratio no doubt decreases the attainable maximum temperature, but increases the partial pressure of carbon dioxide and water vapor, hence increases heat transfer.

(3) *Tube spacing*

Generally tubes are placed in one or two rows in radiant section. More than two rows are not opted due to the following reasons :

- (a) the cost of structure support of such rows is prohibitive,
- (b) Maintenance cost shoots up,
- (c) It is seen that third row absorbs only 8% of heat transfer, while first and second rows absorb more than 90%. Thus the amount of heat transfer is not economically balanced with the overhead charges.

To clarify further, number of rows bring about blanket-effect and all the tubes cannot see the flame ; hence a single row is even regarded as sufficient. The spacing of two tubes is measured by center to center distance. Experimental studies showed that when the tubes were spaced at larger distances, the heat transfer was more. In general, in the furnace, the tubes are spaced at a distance of 2 to 3.5 times outside diameter (OD) of



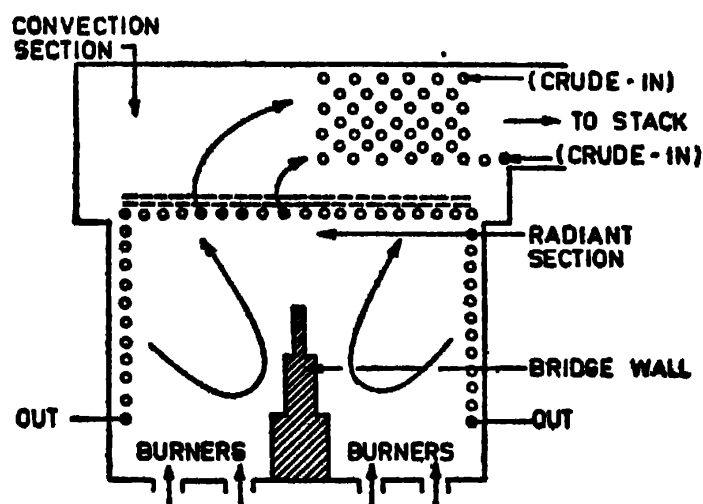
(a) Box Type

FIG. 3.3 Types of Furnaces

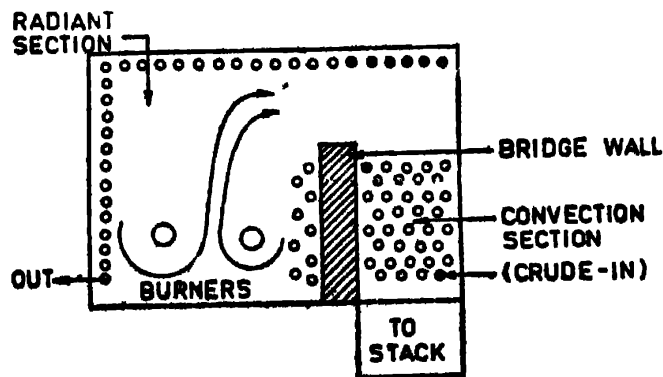
the tubes. It may be seen that 5 tubes of 5 cm OD spaced at 2 OD distance will absorb the same amount of heat as 6 tubes spaced at 1.5 OD. So an optimum tube spacing can reward the designer.

(4) *Over Burdened tubes*

Some of the tubes (blackened ones in Fig. 3.3) receive heat from radiation as well as from convection, as the gases pass over this bank of tubes. This way the tubes receive more heat than they can bear or is required. Such over heating exacerbates coke formation and for this reason, these tubes are utilised for super-heating purposes.



(b) Separate Convection Type



(c)

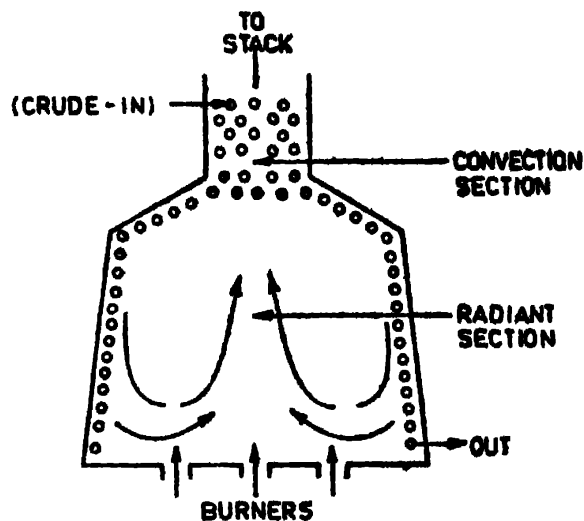
(c) Down Convection Type

FIG. 3.3 Types of furnaces

(5) *Cross over temperature*

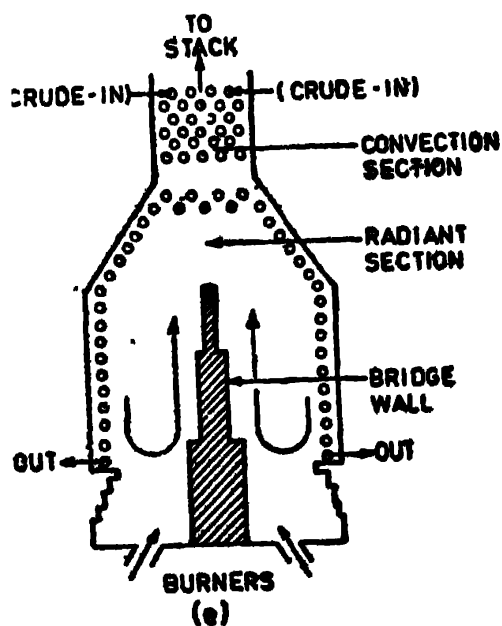
The net amount of heat transfer in radiant section is dependant upon the available temperature of the gases. Modern fur-

aces extract 60—70% of the net heat available, in radiant section alone. So the temperature of the gases leaving the radiant section has to be calculated from heat balance.



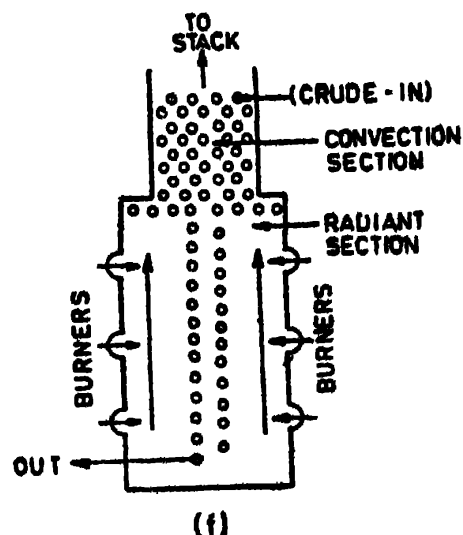
(d)

(d) Kellog Type



(e)

(e) Up Fired (U.O.P.) Type



(f)

(f) Radiant Type

FIG. 3.3. Types of Furnaces

As was mentioned earlier, the convection zone is situated away from the radiant zone, the passage leading from radiant section to convection section is called 'duct'. The duct opening is

usually $1/3$ of the width of the furnace in rectangular type, and the convection section is placed directly on radiant section ; for circular type or separate convection type or down convection type it is better to calculate the duct area on the basis of flue gases generated.

(6) Combustion volume

Radiant section volume depends upon the fuel-air ratio. However, it is customary to express in terms of heat release. For moderate heating rates, furnace volume of one cubic meter is required for 28,000 Kcals (11.7×10^4 Kjoules) heat release per hour. For severe operations heat density may exceed this rate upto two times.

For a satisfactory design, the following schedule of heat distribution may be employed :

Convection heat transfer	—	30—35%
Radiant heat transfer	—	45—60%
Losses (furnace)	—	5%
Stack losses	—	12%

TABLE 3.2 HEAT DUTY FOR VARIOUS OPERATIONS

	Projected area basis Kj/hr.Sq.meter	Velocity M/Sec.
Topping operations	25—50 $\times 10^4$	2.5
Vacuum distillations	25—30 $\times 10^4$	2— 2
Mild cracking	14—20 $\times 10^4$	2— 3
Severe cracking & coking	25—35 $\times 10^4$	2— 3
Treatment operations	20—25 $\times 10^4$	1— 2
Cracking of gases for olefins	13—16 $\times 10^4$	8—10

Design of a furnace is based upon Hottle, Wilson method and radiant heat absorption is given as¹¹ :

$$R = \frac{1}{1 + \frac{G\sqrt{Q/aA_s}}{S}} \times 100 \quad (3.2)$$

where R = % heat absorbed in radiant section

G = Air : Fuel ratio (Wt. basis)

α = Factor to convert actual exposed surface to cold surface 0.986 for two rows at spacing $2.0D$

if Q is in Kj/hr, $S = 14200$ (Area in M^2)

if Q in Btu hr⁻¹, $S = 4200$ (Area in ft^2)

if Q in Kcal hr⁻¹, $S = 6930$ (Area in M^2)

A_o = Area of wall having tubes in front of it.

The trend of α is shown in figure 3.4, depending upon the number of rows of tubes and pitch distance between tubes, the factor varies,¹² for one row of tubes at pitch distance $2D$. α is equal to 0.88 and for two rows for same pitch it is 0.986. When more than one row is present, α factor can be estimated to total number of rows or each individual row to total rows. When two rows are there, the first row (nearest to wall) will have an $\alpha = 0.69$ while the next row will have α equal to 0.3.

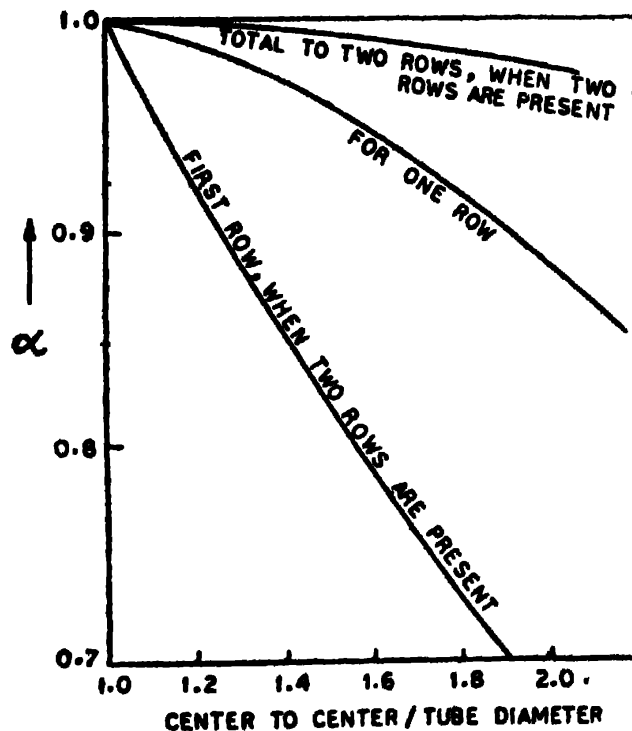


FIG. 3.4 α -variation with Tube Spacing and number of Rows

When area of wall (A_o) with mounted tubing in front of it is calculated, it is obviously immaterial how many rows are present as they do not change the significance of arrangement.

Lobo and Evans¹³ method gives a good procedure for checking the furnace performance which is already in working condition but, it is seldom used for design (method) calculations.

The remaining heat from the gases going out of radiant section is significantly extracted in convection zone.

Convection section resembles any other heat exchanging system, and the design data of such equipment¹⁴ may furnish valuable information. Unlike radiation coefficient, convection coefficient depends upon many factors and the coefficient derived by conventional methods does not include the effects of unremitting^{15,16} radiation, prevailing in the furnace. The first row of convection section is usually submitted to such situation which leads to incredibly high heat transfer rates. Monrad's^{17,18} empirical relation for convection coefficient is presented in eq. 3.3.

$$h_o = \frac{2.845 G^{0.667} \times T^{0.8}}{D^{0.88}} \quad (3.3)$$

where G = mass flow rate $\frac{\text{kg}}{\text{sec. } M^2}$

$T = ^\circ K$

D = outside dia of tube, cms.

3.2.3 LOBO-EVANS METHOD

Working of a furnace is checked by this method. Despite it looks as an empirical one, it incorporates all the factors that influence radiation. In Hottel's equation 'S' factor includes some of the factors that aid radiation, however the effects of radiation constituents and emissivity factor are not properly augmented. The check by Lobo-Evans method consists of the following steps :

- (a) α -factor is evaluated,
- (b) Area of wall that carry the tubes is evaluated
- (c) With the known characteristics of fuel and air-fuel ratio, partial pressure (p) of carbon dioxide and water vapor is found out. Fig. 3.5(a)
- (d) Assuming adiabatic flame temperature as equal to bridge wall temperature, tube skin temperature is found out.

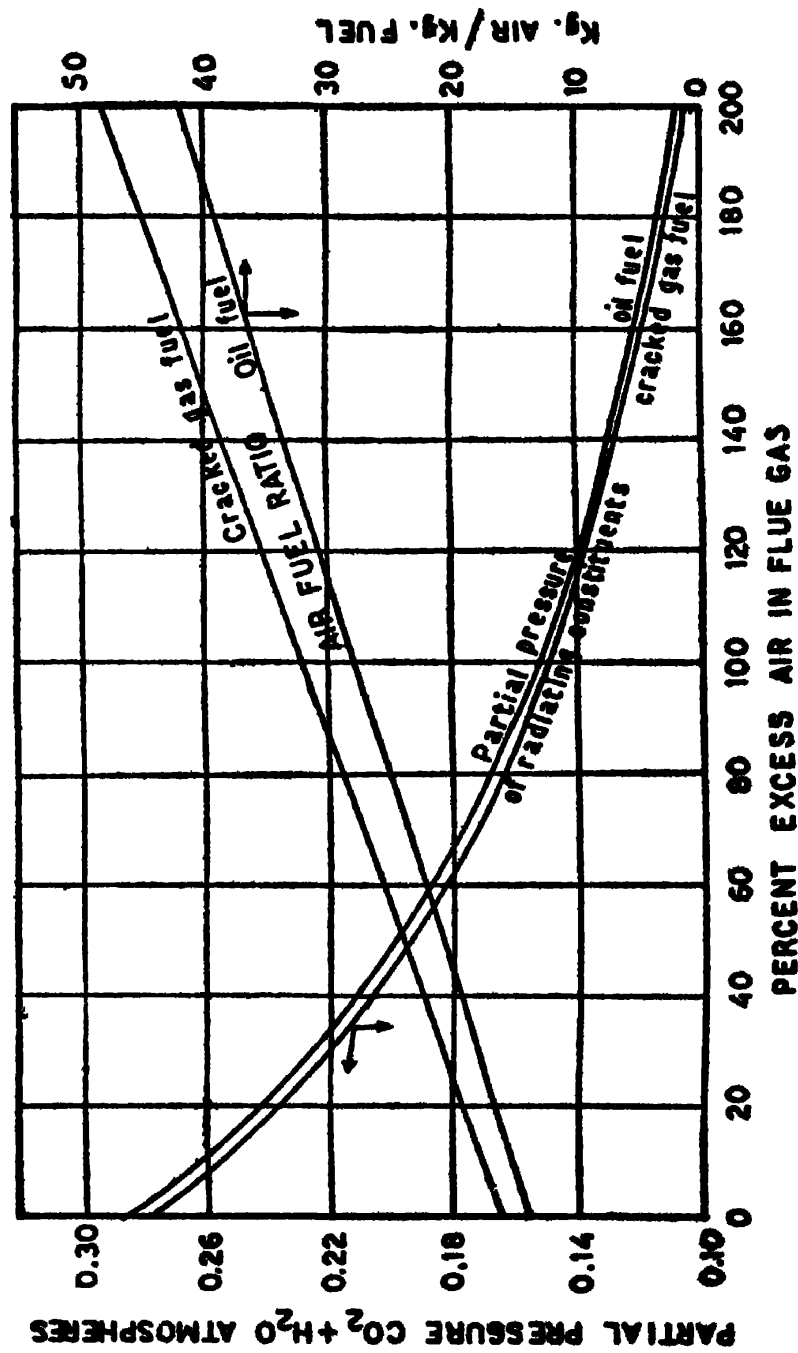


FIG. 3.5a Combustion data on cracked-gas and oils fuels
Lobo and Evans, (*Trans. A.I. ch.E.*)

- (e) Flame emissivity is related to partial pressure of radiant constituents (gases) and mean radiant beam length (L) [Fig. 3.5(b)]

Mean length of radiant beam is dependent on the geometry of the furnace.²⁰

For rectangular type of furnace where length : breadth : height ; dimensions are in the ratio of 1 : 1 : 1 to 1 : 2 : 4 ; Then

$$L = 1/3 \sqrt[3]{\text{vol. of furnace}}$$

for circular furnaces $L = 1/2 D$, where height is many times diameter.

Effective Refractory Area (AR) is the total wall area less the effective surface αA_o .

- (f) Exchange factor¹⁴ is evaluated²¹ in terms of flame emissivity and ratio of $AR/\alpha A_o$ [Fig. 3.5(c)]

- (g) Rate of heat absorption (Q_r) is given by $\frac{RQ}{\alpha A_o Q}$;
by assuming 'R' a fraction of total heat release (Q), this can be calculated.

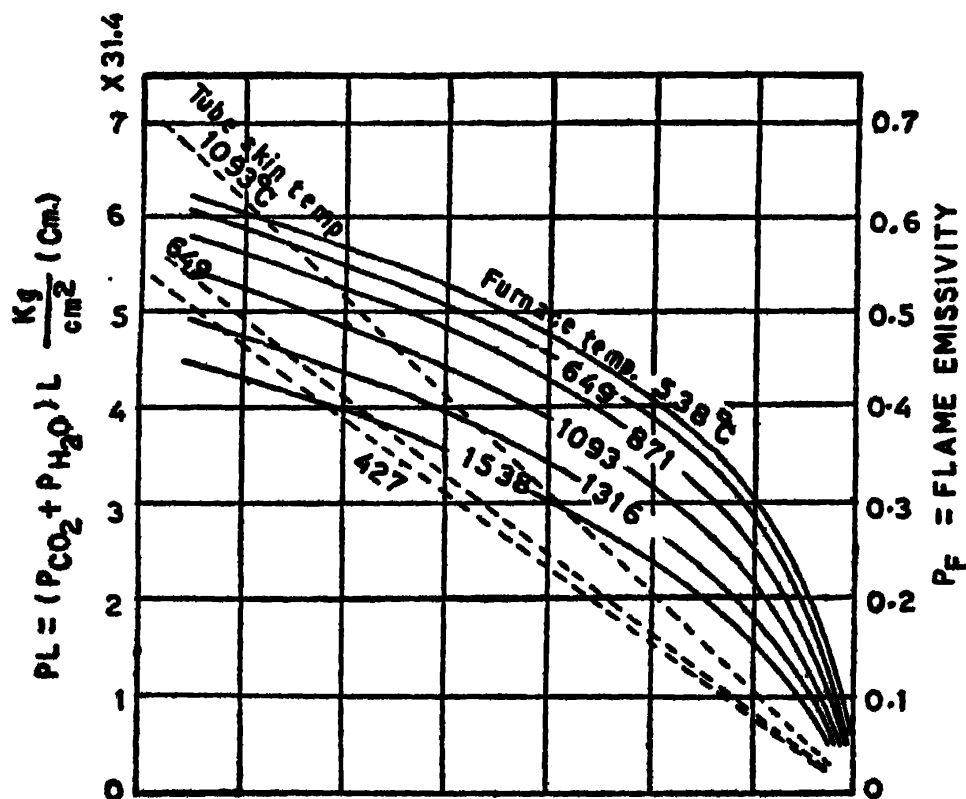


FIG. 3.5b Flame Emissivity
Lobo and Evans, (*Trans. A.I. ch.E.*)

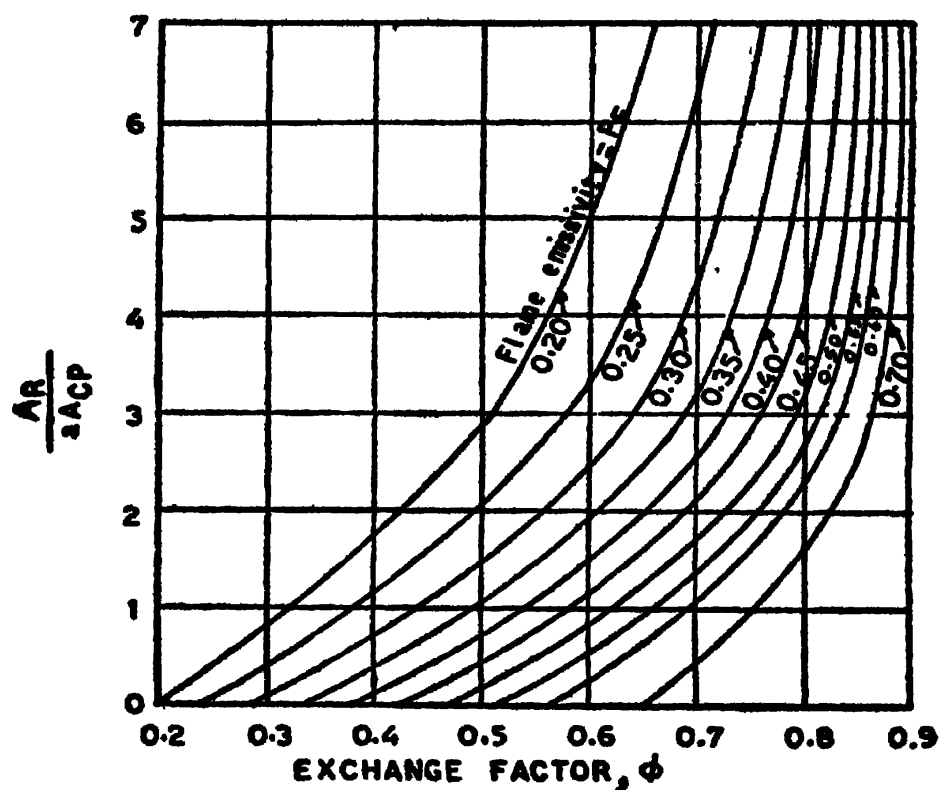


FIG. 3.5c Over-all Exchange factor
Lobo and Evans, (*Trans. A.I. ch.E.*)

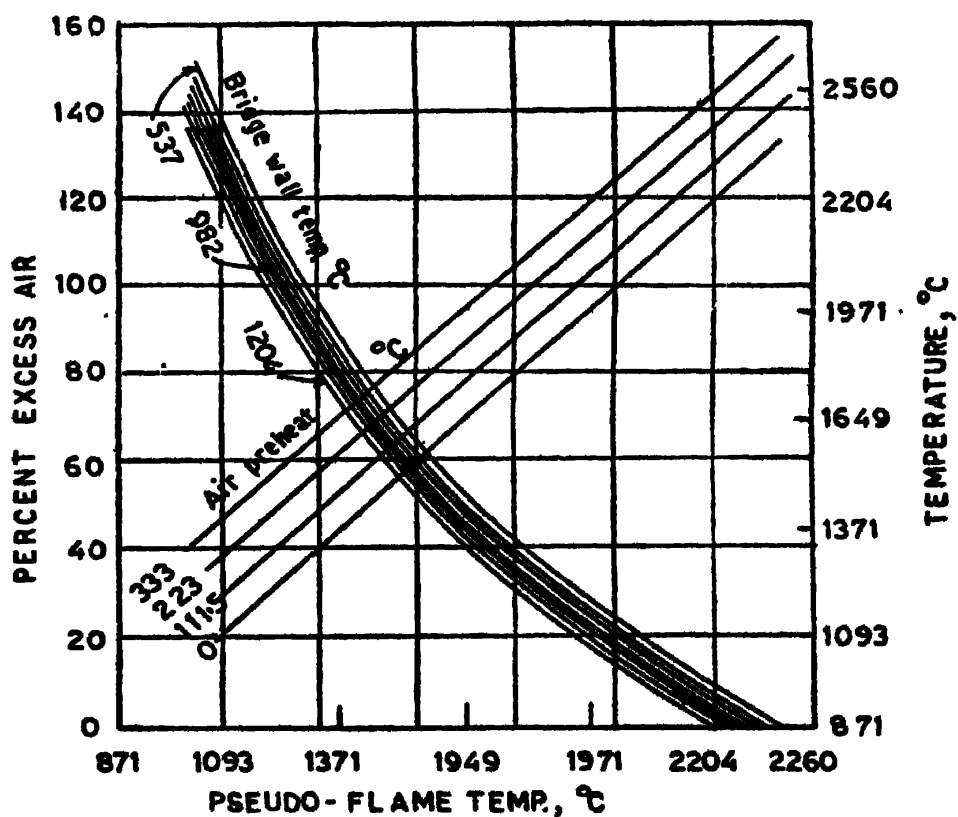


FIG. 3.5d Pseudo flame temp. for cracked-gas fuels
Lobo and Evans, (*Trans. A.I. ch.E.*)

Checking of gas temperature, (which was earlier assumed as the bridge wall temperature) is carried out on the basis of equation (3.1). The gas temperature, Pseudo flame temperature and tube skin temperature are obtained from Fig. 3.5 (d). Gas temperature thus found should not differ more than $\pm 54^{\circ}\text{C}$.

Problem 3.1

A petroleum stock at a rate of 1200 bbl/hr. of sp. gr. 0.8524 is passed through a train of heat exchangers and is allowed to enter directly the radiant section of box type heater at 220°C . The heater is designed to burn 3,500 kgs per hour of refinery off gases as fuel. The net heating value of fuel is $47.46 \times 10^8 \text{ K}_j$ per kg. The radiant section contains 150 sq. meters of projected area of one row of tubes (10.5 cm OD, 12 m long and spaced at 2 OD)

Find the outlet temperature of the petroleum stock,

Data $\alpha = 0.88$

Air fuel ratio = 25

Average Specific heat of stock = $2.268 \text{ K}_j/\text{Kg}^{\circ}\text{C}$.

Solution

$$\text{Total heat liberated} = 47.46 \times 10^8 \times 3,500$$

$$= 1.66 \times 10^8 \text{ K}_j \text{ per hour}$$

$$\text{Projected area of one tube } (L \times D) = 12 \times 0.105$$

$$\text{No. of tubes} = \frac{150}{12 \times 0.105} = 120 \text{ tubes}$$

$$\alpha A_o = 0.88 \times 120 \times 0.105 \times 2 \times 12 = 266 \text{ Sq.m.}$$

$$\text{Heat absorption \% } (R) = \frac{1}{1 + 25 \sqrt{\frac{1.66 \times 10^8}{266}}}$$

$$= 44\%$$

Outlet temp. of the stock :

$$MC_p \Delta t = Q$$

$$1200 \times 200 \times 0.8524 \times 2.268 \times \Delta t = 0.44 \times 1.65 \times 10^8$$

$$(\text{bbls} \times \text{liters} \times \text{sp.gr.} \times \text{sp.heat} \times \text{temp.difference})$$

$$t = 157^{\circ}\text{C}$$

So the outlet temp. is equal to $157 + 220 = 377^{\circ}\text{C}$

Problem 3.2

Crude oil of the same characteristics of Problem (Chapter 2). No. 2.1 is to be heated in pipe still heater. The crude enters the convection section at 100°C and then enters the radiant section at a rate of 1000 bbls/hr. Maximum temperature of the crude at outlet is 350°C.

- (a) Find the area of convection section and radiant section.
Estimate vol. of furnace.
- (b) Calculate the pressure drop in the furnace
- (c) What is the cross over temperature ?
- (d) Show the arrangement of tubes in radiant section

Assume 30% Heat transfer in convection
18% Heat losses.

Sp. gr. of crude = 0.8570

Sp. heat of crude = 0.67 cal/gm°C

Fuel net heating value : 13,000 Kcals/Kg.

Radiant heat transfer rate : 17×10^4 Kj/Sq. meters
(on projected area basis)

Average sp. heat of flue gases : 1.28 Kj/Kg°C

Solution

Total heat liberated by fuel = Heat to raise the temp.
of crude + latent heat + losses.

$$\begin{aligned} \text{Heat for raising the temp. of crude from } 100^\circ\text{C to } 350^\circ\text{C} \\ &= 1000 \times 200 \times 0.8570 (350 - 100) (0.67) \\ &= 297 \times 10^5 \text{ Kcals or } (1243.46 \times 10^5 \text{ Kj}) - (a) \end{aligned}$$

Latent heat is to be calculated on the basis of percentage vaporisation obtained from the TBP curve of this crude. Fractions, whose boiling point is below 350°C will vaporise. Hence the latent heat for such fractions has to be found out as shown in Table 3.3

(a) From Table 3.3 latent heat 94.22×10^5 Kcals - (b)

Heat duty $(a+b) = 391.22 \times 10^5$ Kcals/hr.

with losses 18% total =

heat duty $(Q)_a = 461.61 \times 10^5$ Kcal/hr.

or

1932.77×10^5 Kj/hr.

Amount of fuel required

$$= \frac{461.61 \times 10^5}{13,000} = 3552 \text{ Kgs/hr}$$

Feed outlet temperature in convection is roughly calculated as

$$\begin{aligned} & \text{Total temperature difference} \times \% \text{ Heat transfer} \\ & \text{in convection} \\ & = (350 - 100)(0.30) = 75^\circ\text{C} \\ & \text{i.e. } 100 + 75^\circ\text{C} = 175^\circ\text{C} \end{aligned}$$

The outlet of the feed in convection section is 175°C . % evaporation upto this temperature from 100°C is 11.7. This amount of crude is kept in liquid state by applying pressure. The pressure required is obtained from the nomogram Fig. 2.2a (Chapter 2).

Convection Section

$$\begin{aligned} \text{Sensible heat from } 100^\circ\text{C to } 175^\circ\text{C} &= 89.1 \times 10^5 \text{ Kcals} \\ \text{Latent heat (11\%)} \text{ Vaporisation} &= 42.28 \times 10^5 \text{ Kcals} \\ \text{Total heat} &= 131.38 \text{ Kcals} \\ &\text{or } 551.8 \text{ KJ.} \end{aligned}$$

Remaining heat is absorbed in radiant section

$$\begin{aligned} \text{Total heat} &: 391.22 \times 10^5 \\ \text{Convection heat} &: 131.38 \times 10^5 \\ (Q_r) &= 259.84 \times 10^5 \\ &\text{or } 1091.33 \times 10^5 \text{ KJ} \end{aligned}$$

$$\begin{aligned} \text{Area of tubes} &= \frac{Q_r}{0.15 \times 15 \times \pi} = 91 \text{ tubes} \\ &\text{(length assumed 15 meters Dia 0.15 m)} \end{aligned}$$

Volume of furnace—(I)

$$\begin{aligned} \text{Appropriate heat density per cubic meter} \\ &= 12 \times 10^4 \text{ Kcals.} \end{aligned}$$

$$\begin{aligned} \text{So, vol. of furnace : } \frac{\text{Total heat}}{\text{Heat density}} &= \frac{193277 \times 10^5}{12 \times 10^4} \\ &= 1610 \text{ cubic meters.} \end{aligned}$$

Arrange tubes as

30+30+31 i.e. 30, 30 tubes on side walls and 31 tubes
on top wall

Spaced at 2 OD and providing excess space for two
more tubes on side walls

$$\text{Wall height} = 32 \times 0.15 \times 2 = 9.6 \text{ m}$$

$$\text{Width of furnace} : 31 \times 0.15 \times 2 = 9.3 \text{ m}$$

$$\text{Length of tube} : 15 \text{ m.}$$

In the roof of furnace a length of 2.0 meters is reserved as opening for convection section inlet, this space is utilised for superheating purpose.

$$\text{So total width} : 2.0 + 9.3 = 11.3$$

Furnace volume checked by this arrangement

$$= 9.6 \times 11.3 \times 15 = 1595 \text{ meters}^3$$

which is comparable with figure (I).

In convection section, the area is calculated on the basis of average convection heat transfer coefficient. Convection coefficient is evaluated by knowing the flue gas velocity

$$\text{Amount of fuel burnt} = 3552 \text{ Kgs/hr.}$$

$$\text{Amount of air used} = 3552 \times 25 \text{ Kgs/hr.}$$

$$\text{Total amount of gases} : 92,352 \text{ Kgs/hr.}$$

Assuming fuel + excess air as combustion products.

$$\begin{aligned} \text{Flue velocity (mass)} &= \frac{92,352}{\text{Area of convection duct}} \\ &= \frac{92,352}{2.0 \times 15 \times 60 \times 60} \\ &= 0.884 \text{ Kgs per Sq. meter. Sec.} \end{aligned}$$

$$\text{Convective heat transfer } (Q_c) = A_c U_c (LMTD)$$

$$A_c (\text{convective heat transfer area}) = \frac{Q_c}{U_c (LMTD)}$$

Calculation of $LMTD$: See Fig. 3.6.

$$\begin{array}{lll} LMTD : \Delta t_1 = \text{gas temp.} & \text{---} & \text{outlet temp. of} \\ & & \text{crude} \\ & \text{inlet convection} & \\ & (t_1) & (T_1) \\ \Delta t_2 = \text{gas temp.} & \text{---} & \text{inlet temp. of} \\ & \text{outlet} & \text{crude } (100^\circ\text{C}) \\ & t_2 & T_2 \end{array}$$

$$LMTD = \frac{\Delta t_1 - \Delta t_2}{2.303 \log \frac{\Delta t_1}{\Delta t_2}}$$

Gas temp. at inlet to the convection section is calculated as shown in part (C) of this problem.

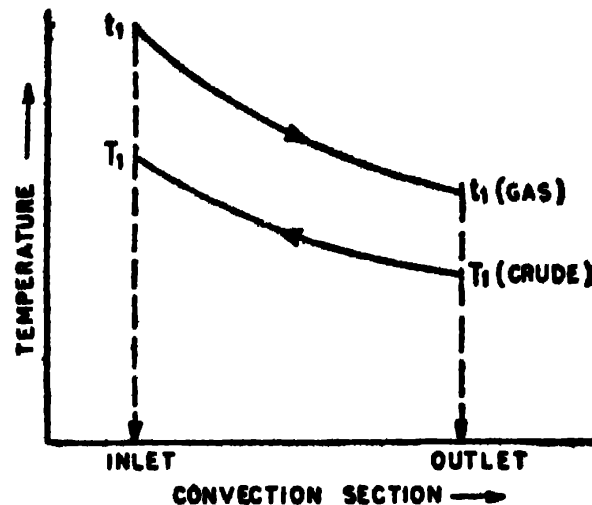


FIG. 3.6 L. M. T. D. Calculation

So : $\Delta t_1 = 695.6 - 175^\circ \approx 520$

Δt_2 = the difference between outgoing temperature of gas and incoming crude should be atleast 200°C to maintain good draft.

$$LMTD = \frac{520 - 200}{2.303 \log \frac{520}{200}} = 334.8^\circ\text{C}$$

U_o is obtained as $85.86 \frac{\text{kJ}}{\text{hr. Sq. m}^\circ\text{C}}$

(Nelson P. 613)

$$\text{Area in convection zone} = \frac{551.8 \times 10^6}{334.8 \times 85.86} = 1920 \text{ Sq.}$$

meters.

$$\text{No. of tubes} = \frac{1920}{\pi \times 0.15 \times 15} = 388 \text{ tubes.}$$

(Area of tube πDL)

(b) Pressure drop in convection section (P_o) pressure drop in radiant section (P_r) + Pressure to be imposed to restrict vaporization (P_f)

Total pressure drop due to friction

Mass velocity of crude at

$$\text{inlet conditions} = \frac{1000 \times 200 \times 0.8570 \times 4}{3600 \times \pi \times (0.15)^2}$$

$$\text{Velocity of crude} = \frac{1000}{3600} \times \frac{200 \times 4}{\pi \times (0.15)^2 \times 10^3} = 3.2 \text{ M/sec.}$$

$$\text{Reynolds No.} = \frac{3.2 \times 0.15 \times 857}{0.01 \times 10^{-4}} = 4.1 \times 10^6$$

(μ is viscosity 0.01 Cst at average temp.)

Reynolds no. shows that the flow is in highly turbulent region.

$$P_e + P_r = \frac{4fLV^2}{2g_c D} \quad \text{where } f : \text{Fanning friction factor} \quad (.005)$$

L : length of tubes

V : velocity of liquid

g_c : 9.81 m/sec²

$$= \frac{2 \times .005 (3.2)^2 \times 15 (91 + 272)}{0.15 \times 9.81} = 375.7 \text{ meters}$$

or 32.2×10^4 Kgs/Sq.meter.

Total pressure at which liquid is to be pumped into the furnace : $P_e + P_r + P_f$

(To simplify two phase flow, it has been assumed that under a pressure of P_f , the crude evaporation may be neglected, hence liquid volume is taken into consideration)

Back pressure required in convection and radiant sections :

The outlet temperature of convection section is 175°C % evaporation upto 175°C from 100°C = 11.7%. This 11.7% of crude should be kept in liquid state by imposing pressure i.e. operating under pressure. The back pressure required in convection section is obtained from the nomogram Fig. 2.2a (Chapter 2) is equal to 11.2×10^4 Kg/Sq.meter

Similarly for radiant section (nearly evaporation takes place from 175°C—350°C) is equal to 28×10^4 kgs/M²

So the total pressure in the furnace

$$= 11.2 \times 10^4 + 28 \times 10^4 + 32.2 \times 10^4 \\ 71.4 \times 10^4 \text{ Kgs/Sq.meter.}$$

(c) Cross over temperature :

This is obtained by heat balance¹⁰ in the radiant section :

TABLE 3.3
FROM T B P ANALYSIS

Fraction	B. P. °C	Vol. %	API	Average mol. wt.	Latent heat Kcal/Kg	Sp. gr	Total heat ($\times 10^4$) Kcal/
Losses		0.47					
LSR	C ₅ -93	3.28	69.6	80	--	0.7035	
Cat. Reforming feed	93-176.7	11.71	46.9	120	65	0.7932	120.748
Heater oils	176.7-226.6	30.61	34.8	200	58	0.8508	302.098
Furnace oil	226.6-326.7	13.69	31.3	230	55	0.8692	292.668
Light FCU Feed	326.7-365.5	9.05	29.0	260	42	0.8816	226.680
Heavy FCU Feed	365.5-543.3	26.97	28.1	--	--	0.8865	--
Reduced Crude	7543.3	4.22	20	--	--	0.9340	--
							<u>942.196$\times 10^4$</u>

Latent heat required for vaporising of crude from 100-350°C
(65.06%) vaporisation

Total heat developed—Heat absorbed in radiant section—
losses in radiant section = Heat going to convection section

Assuming 1% heat losses in radiant zone.

$$\text{i.e. } 1932.77 \times 10^3 - 19.32 \times 10^3 - 1091.33 \times 10^3$$

$$= mc_p \Delta t.$$

$$= 92.352 \text{ Kgs/hr}$$

m = total flue gas

c_p = Sp.heat

Δt = difference in temp.

i.e. $\Delta t = 695.6^\circ\text{C}$ i.e. 665°C above room temperature

(d) Arrangement²² is shown in Fig. 3.3(a).

3.3 Distillation of Petroleum

Distillation is a separation technique used for separation of soluble liquid mixtures into individual components. Petroleum being a mixture of hydrocarbons has a boiling range of -160°C (methane) to $+1000^\circ\text{C}$ or more (pitch) i.e. to say a mixture of gas, liquid and solid, requires an effective and economic distillation to process into a number of cuts of small boiling range. These cuts are later processed and tailored to suit the requirements of consumers. Modern refinery techniques have meticulously laid the way to recover as many fractions as possible from crude, discarding the least possible in view of the binding situation i.e. dearness of crude.

The fractions in demand are in fact the property of a country; (although most of the fractions are common and in good demand, though not to same extent), hence a refinery should have the facilities for such fractions; this in turn makes each refinery a complete entity.

It may be mentioned, a country like the USA is deeply involved in production of more gasoline; frequently converting 70% of crude to gasoline. Whereas in a country like India, the picture is different, the accent being on middle distillates. This necessity has made Indian refineries to exalt the production of more middle distillates. It is true that the nature of crude plays an indecorous role in displaying the characteristics of its fractions, often defeating the aims of refiners. Present and future demands, future expansion, conservation of stocks etc.

are some irksome spells, and a refiner has to give deep thought for all anticipated situations.

The basis of refinery distillation²² design rests completely on TBP tests. Distillation of crude mainly takes place in two stages. First stage distillation is carried out at atmospheric pressure, hence the name 'Atmospheric Distillation unit' (ADU) is conferred on it. The undistilled portion of crude, called reduced crude is further distilled under reduced pressure in a second unit known as 'Vacuum distillation unit' (VDU). The maximum pressure in an atmospheric column seldom reaches two atmospheres and at the top of the column the pressure is only few centimeters of mercury above atmospheric pressure. These two columns differ from conventional towers in practice in a peculiar and conspicuous way by not providing any reboiler. This has been overcome by heating the feed to maximum permissible temperature only once and allowing it to flash in towers. The maximum temperature allowed in topping operations is 375°C. Higher temperatures are not permitted due to degradation of crude by thermal cracking.

When the crude contains a good amount of soluble gases, to avoid load on ADU, a preflashing or topping column is employed. Preflashing is also useful when crude has to be transported to a long distance. Light-ends-free crude gives no problem in transportation. A crude containing less than 6% light ends (gases) usually offers no problem in transportation. Preflashing is conducted at 100°C under a pressure of 3-5 atmospheres to remove these light ends.

3.3.1 *Arrangement of towers*

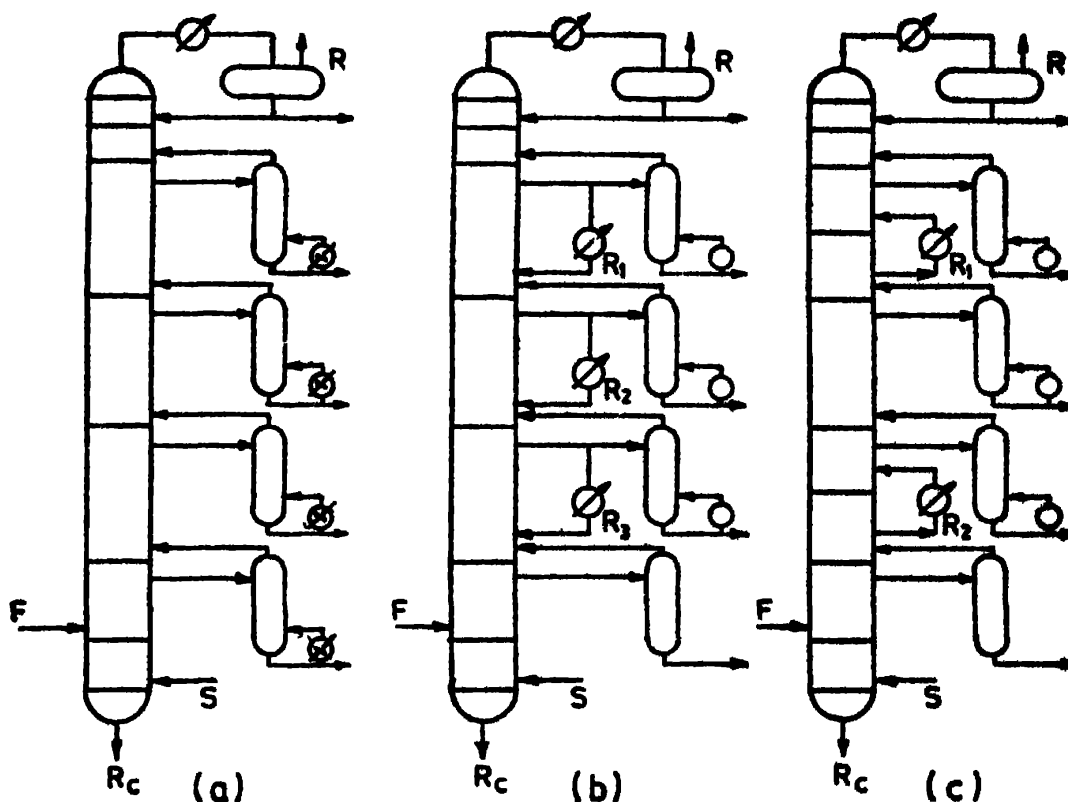
Distillation or flash vaporisation is conducted in two units in series, when it is known as two stage distillation unit. Seldom do stages exceed three. These towers are classified into three distinguished types²⁴:

Fig. 3.7 shows the arrangements of these types viz.,

- (a) Top tray reflux,
- (b) Pump back reflux, and
- (c) Pump around reflux towers.

3.3.1.1 Top tray reflux

This tower has reflux at the top tray only and the reflux is cooled and sent into the tower. Fig. 3.7(a). This defies reflux on any other plate. Consequently, heat input to column is through crude (bottom) and removal is at the top. This creates



F - FEED, S - STEAM, R - REFLUX CONDENSER, R_1, R_2, R_3 - REFLUX
R - REDUCED CRUDE

FIG. 3.7 Arrangement of Distillation Towers

(a) Top Tray Reflux, (b) Pump Back Reflux (c) Pump Around Reflux

always 'a build up of vapor' necessitating larger tower diameters. Obviously the reflux is not proper and quality of fractions is not satisfactory. Economic utilisation of this heat is also not possible. However, the unit is simple in design and operation. But quality of fractions cannot be sacrificed for obvious reasons. Hence in practice this type of arrangement is not preferred.

3.3.1.2 Pump back reflux (Fig. 3.7(b))

In this arrangement reflux is provided at regular intervals. This helps every plate to act as a true fractionator, due to the fact that there is always good amount of liquid. The tower is

uniformly loaded, hence a uniform and lesser diameter tower will do. The heat from external reflux can be utilised, as it is at progressively higher temperatures. However, the design and operation of such towers are costly, but provides excellent service. Most of the refineries are based on this arrangement.

3.3.1.3 *Pump around reflux (Fig. 3.7(c))*

In this arrangement, reflux from a lower plate is taken, cooled and fed into the column at higher section by 2 to 3 plates. This creates a local problem of mixing uneven compositions of reflux and liquids present on the tray. To overcome these ados, designers treat all the plates in this zone as one single plate, the result of which is reflected on the height and number of plates in the column. Usually this pump around is not placed more than at two sections in a column.

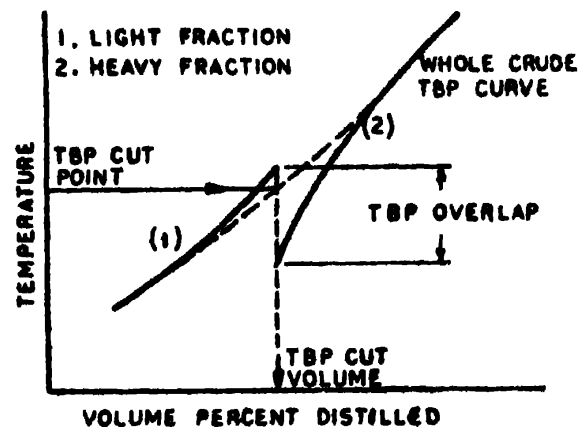
Fig. 3.7(b) shows a distillation unit with four side draws using pump back reflux. The number of side draws in an atmospheric column may go upto eight.²⁵ Side stream strippers are provided to all fractionation units, to ensure quality and close control of products to specification limits.

3.3.1.4 *Design aspects*

Design of atmospheric column is based upon experience, intuition and empiricism. Because of the unpredictable nature of crude, this type of design has been developed. Crude, even though it contains innumerable components, they fall into small close boiling cuts and so individual separation is not possible; hence the design is significantly based upon the TBP and EFV data. Modern towers operate with remarkable accuracy and match with any critically designed tower. Adoptability of resembling crudes and marginal adjustments in quality of cuts are some of the flexibilities of these towers. Further, control by conditions and quality of reflux, along with other operational parameters contribute much towards desired product pattern.

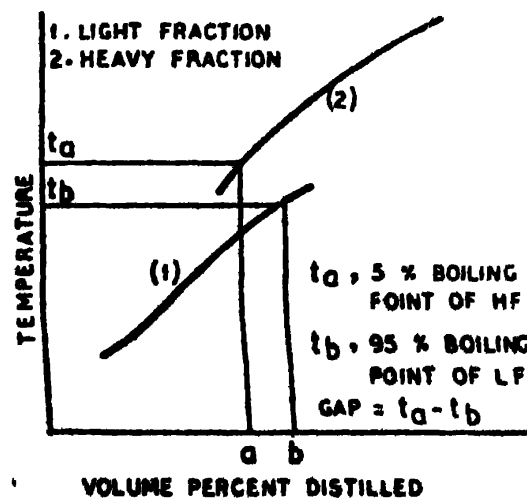
Edmister,²⁶ Packie,²⁷ Watkins²⁸ have furnished valuable literature for designing atmospheric and vacuum towers. Packie's classical work showed the trails of chemical engineering principles, though expressed in a different terminology. Accordingly, the design is based upon two terms, namely, Degree of separa-

tion" and "Degree of Difficulty of Separation". Degree of Difficulty of separation is more or less connected with the purity of products. With increasing closeness of boiling points of two cuts, separation becomes a difficult task. So it is expressed as the difference between the ASTM 50% boiling points of two successive cuts. Obviously larger difference renders separation easier. Degree of separation is encountered in separation of two close boiling cuts, irrespective of the attainable purity. It is otherwise closely resembling relative volatility. ASTM gap is defined as the difference between 5% boiling point of heavy fraction and 95% boiling point of preceding cut. When ASTM gap is not available TBP overlap may be taken into account.



(a)

FIG. 3.8 (a) T.B.P. Overlap and Cut Point



(b)

FIG. 3.8 (b) A.S.T.M. Gap

TBP overlap is the simple difference between FBP and IBP of successive fractions. These are explained in Fig. 3.8(a) & (b).

Packie's method is based upon these gaps and overlaps. The number of plates in a particular section depends upon the gap and reflux ratio. Separation capability is denoted by 'F' factor ; given as²⁹ :

$F = \text{reflux ratio} \times \text{number of plates in that section}$. This F is related to ASTM 50% difference of fractions (successive) and the gap of these fractions, as shown in Fig. 3.9.

EFV curve obtained at normal^{30,31} pressure should be converted to flash zone pressure ; from this corrected EFV curve, above-mentioned gap and 50% difference should be found out, for all the fractions. In practice a good quantity of steam is utilised during distillation, steam being inert causes the reduction in partial pressure of hydrocarbons in the tower. Reduction of partial pressure of hydrocarbons may contribute to a temperature drop³² of 10-20°C in distillation columns and side stream strippers³³.

The hot crude, where it is flashed in column is called flash zone and significance of flash zone is immense due to the following facts :

- (a) Increase in flash zone pressure increases draw temperatures.
- (b) Increase in over-flash decreases the side draw temperatures from the second draw onwards. [Overflash is that portion of total vapor leaving the flash zone boiling above the nearest side draw fraction ; but never included in that fraction. Over flash allowance is kept to an extent of 2% total crude processed in column. This maintains a good pool of liquid and reflux on plates. The outlet of this overflash is mostly from the bottom of the column].
- (c) Increase in steam in flash zone decreases the product temperature.
- (d) Pressure in flash zone is reflected throughout the column in the form of plate temperatures. Increase in this pressure demands more quantity of steam to maintain the designed pattern. It may be

stated that while distilling heavy crudes a reduction in flash zone pressure furnishes a good yield of products, without this one has to be content with the yields of products as shown by EFV curve at that pressure.

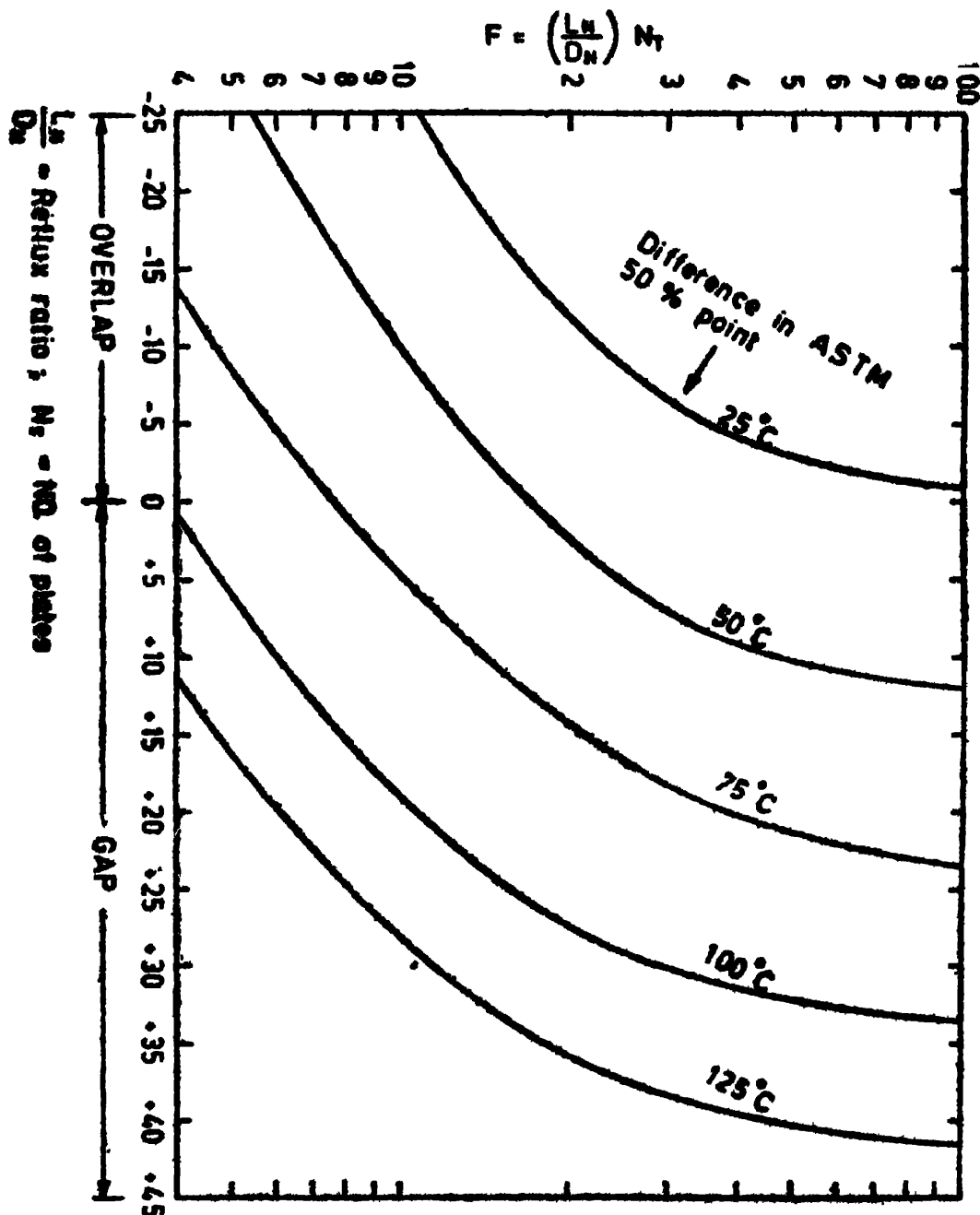


FIG. 3.9 F-Factor & ASTM Gaps

From Petroleum Refinery Distillation, Second Edition, by R. N. Watkins, Copyright (c), 1979 Gulf Publishing Company, Houston, Texas used with Permission.

ASTM gaps followed in practice

Light naphtha to heavy naphtha	12 to 18°C
Heavy naphtha to light distillate	15 to 30°C
Light distillate to middle distillate	2 to 6°C
Middle distillate to first draw	2 to 6°C

3.3.2 ATMOSPHERIC DISTILLATION UNIT (ADU)

All distillation towers are plate type towers. The arrangement of plates and tray hydraulics are not discussed here. All types of conventional trays like bubble-cap plates,⁸⁴ ballast trays, valve trays, sieve plates^{85,86} etc. are in service. Usual dimensions and operating data are given below for an Atmospheric column :

Tower diameter	— 5 to 8 metres
Number of plates (depends on no. of draws)	—25 to 40
Maximum allowed pressure drop per plate	0.015 Kg/cm ²
Allowed pressure drop between flash zone to top of tower	0.5 to 0.55 Kg/cm ²
Pressure drop from furnace outlet to flash zone	0.3 to 0.4 Kg/cm ²
Pressure at the top of the tower	—1.20 to 1.4 Kg/cm ² (abs)
No. of plates required for separation	
Light naphtha to heavy naphtha (80°—130°C)	6 to 8 plates
Heavy naphtha to light distillate (180°C)	5 to 6 plates
Light distillate to middle distillate (250°C)	4 to 6 plates
Middle distillates to gas oil (diesel) 330°C	3 to 4 plates
Flash zone to first draw	3 plates
Flash zone to bottoms	3 plates
Tower top temperature	100—110°C
Reflux drum pressure	1.1 to 1.15 Kg/cm ² (abs)

Steam rate per barrel of crude	4 to 5 Kgs
Reflux ratio for light fractions	2 to 3
Reflux ratio for heavy fractions	1.5 to 2.5

Top of the ADU is fitted with reflux condenser. Gases at equilibrium with light naphtha will escape, leaving a mixture of two layers comprising of light naphtha and water. Water is drained off from this condenser and light naphtha is sent for stabilisation purpose. This reflux condenser usually operates at slightly higher pressure than the atmospheric pressure to condense the vapors.

3.3.3 VACUUM DISTILLATION UNIT

Reduced crude from the bottoms of ADU is further distilled under reduced pressure to get the remaining (or as many) fractions. The bottoms of vacuum distillation column is known as 'Goudron or residuum'.

Design of this tower is more empirical than ADU. The purpose of this tower is clearly defined even before designing. Major alterations are very difficult. Crude certainly dictates its destiny, that is, whether the stock is best for lube oils or best for cracker feed. Number of side cuts are limited to three, may occasionally go upto four. The operation of the tower is more costly than ADU and rests on the economic production of steam. Amount of steam in demand is dependent on the extent of vacuum. So even the design of tray, plays its own role. A plate that gives least pressure drop is well preferred. Steam with vacuum, separates the fractions with a good economy rather than any of them alone. Vacuum alone is used when highly emulsifying crudes are handled, and in such cases, the vacuum is maintained below 15 mm Hg. This type of operation is very costly and hence not practised. Most of the towers operate at a flash zone pressure of 30-40 mm Hg. which gives a top pressure of 20-25 mm Hg. This leaves an overall pressure drop of 10 to 15 mm from flash zone to top plate; this signifies the importance of low pressure drop plates. It is clearly seen, that by placing the partial condensers directly over the head of the column, saves additional piping and minimises the pressure drop in a vacuum column :

Vacuum tower operating data

Temperature of reduced crude at	
at flash zone	350—400°C
Pressure in flash zone	30— 40 mm
„ for long residuums	40— 60 mm
Top pressure	12— 15 mm
Temperature at top	225—250°C
Trays between two draws	3 to 4
Steam (at 370°C) rate	0.3 to 5 Kg per barre
Over flash	2%

Vacuum distillation tower is designed for a limited number of products, and a tower contemplated for one operation may not be suitable for other products. The main products of commercial interest are :

1. Cracking stocks,
2. Fuel oil mixtures (Heating oils),
3. Lube oils,
4. Bitumen.

Towers for the production of cracking stocks require less elaborate fractionation. The temperature of the feed stock may cross even 400°C. All cracking stocks (catalytic) must be free from detrimental metals like vanadium, nickel etc. to avoid catalyst poisoning. Metals and other sulfur, nitrogen bearing compounds may not be that much hazardous, when hydrocracking operations are in progress. To satisfy such requirements, the vacuum tower has to give only one top product and one side product. Bottoms of tower are meant for asphalt making. Towers for such operations are closely packed ; if trays are used, wire mesh screens are inserted between plates. This is very essential, at least around draw plate, to stop the metallic bodies being carried into main product. Towers employed for heating oils do not require much fractionation. However, metallic bodies should be stopped from mixing the main product which alleviates ash content. Two side stream products are usually obtained with difference in gravity to serve light and heavy duty operations. Such towers are preferably fitted with grids or packings. In this case the primary importance goes to the specifications of products rather than mode of operation. When cracked fuel oils are primarily aimed, the long

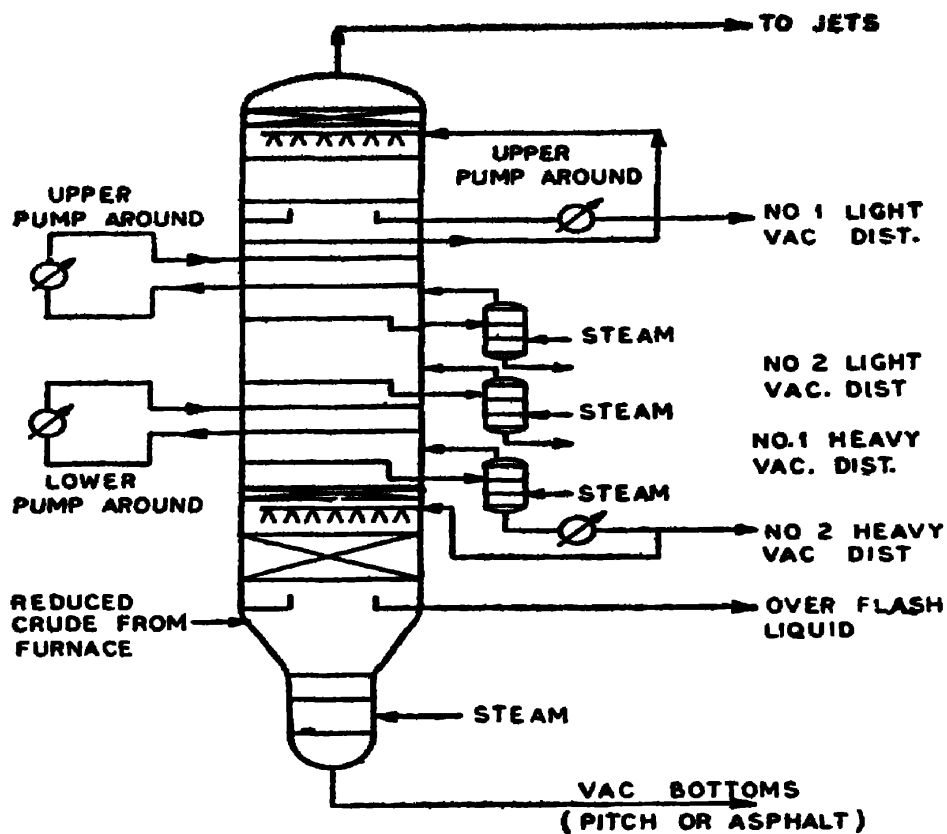
residuum requirement is high, accordingly a moderate vacuum of 60 mm at flash zone is conducive.

Towers devoted for the production of lube oils or waxy distillates employ 3-4 side draws. These are equipped with trays of minimal pressure drop. These towers may be fed with reduced crudes, bright stocks or other lube bearing stocks for close fractionation. Viscosity and flash point specifications are closely guarded. Raw neutral oils produced must have viscosity 77 SUS, and a flash point of 180-200°C. Heavier cuts usually have 140 SUS and flash point 220°C. In all the towers, draw plates are fitted with separators. Lube towers are profoundly fitted with cascade trays. When bottoms are the desirables, deliberately light fractions are allowed to seep into this fraction. This enhances the plasticity of bitumen which enables easy processing.

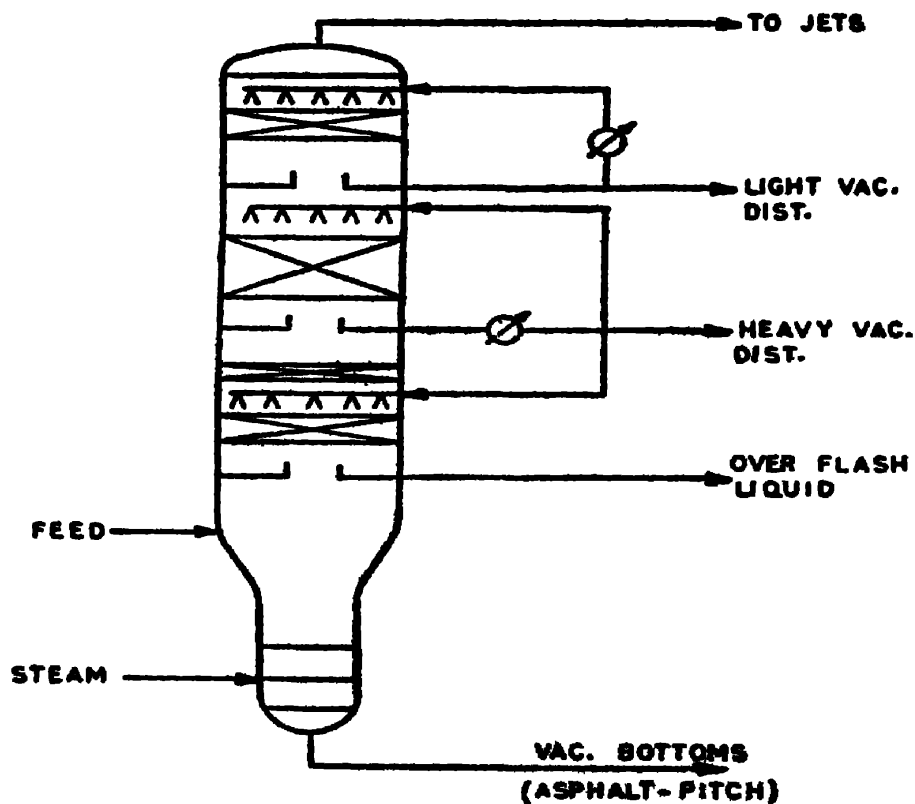
Bitumen is graded by the penetration index. Different applications require different penetration quality, an index in the range of 85 down to 100 is commonly desirable. API gravity, in the range of 5 to 8 is recommended. Though bitumen is mainly separated under the existing conditions of tower, the desirable qualities may not be well anticipated. Further processing of bitumen is always necessary. Vacuum distillation may also be conducted in two stages for effective separation, if speciality oil products are ventured. Fig. 3.10(a)(b) describes the arrangement for different operations.

3.3.4 OVERHEAD CORROSION IN DISTILLATION UNIT

Corrosion in distillation unit is mainly due to hydrogen sulfide and chloride ion. High sulfur and salt containing crudes generally create these problems. Though prior to distilling, desalting of crude is practised, ineffective desalting presents this problem. Slight amount of hydrogen sulfide causes a protective film as iron sulfide, but excess of this leaves sulfide ion and chloride ion as threatening corrosion contributors. P_H of this system is directly proportional to the partial pressure of these components. Chloride ion is mainly contributed by hydrolyzable calcium, magnesium chlorides. If crudes can be desalted to a minute extent of a Kg of salt per 1000 bbls; perhaps resulting acid concentration may not exceed 0.6 Kg. per 1000 bbls, and



VACUUM TOWER FOR LUBES (PUMP AROUND)

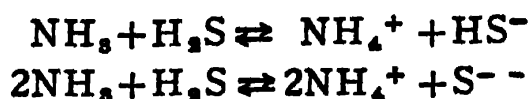


FUELS TYPE VACUUM TOWER

**FIG. 3.10 Vacuum Distillation Column :
(a) Lubes—Type, (b) Fuels—Type**

though it seems to be not much, still it can offer problems under those operating conditions.

Prevention of this type of corrosion is accomplished by sending required amount of ammonia into column. It is also seen that the presence of high amount of ammonium chloride can lead to severe troubles. Even though ammonium chloride is fairly soluble in water and carried away but a concentration above 70 ppm would lead to the appearance of crystals. The amount of ammonia admitted depends largely on P_H of H_2S . The system can be written as⁸⁷



i.e. 2 moles of NH_3 can combine completely if second ionisation constant of H_2S is also taken into consideration. But, it is not necessary, as the ionisation constant is very small.

Ionisation constant (K) for such system can be written as

$$K = \frac{(NH_4^+)(HS^-)}{(NH_3)(\text{Partial pressure of } H_2S)}$$

From which the partial pressure of H_2S can be found out. The system resembles the situation where NH_3 , H_2S and H_2O are present.⁸⁸ Therefore, it is seen that 20 to 30% of H_2S , should be neutralised leaving excess of H_2S ⁸⁹ to form the buffer system $H_2S-NH_4OH-NH_4HS$. That leaves the system at P_H 5.5 to 6.5. Modern practice is to use organic⁴⁰ amines instead of ammonia. Amines are more basic than ammonia and serve without any side effects. These react usually to form soluble compounds with chloride and sulfide ions, thus tendency of crystallisation does not appear. It may be even significant to introduce caustic, if the concentration of sulfur is high.

3.3.5 TOPPING OPERATION

In practice, separation of different fractions from crude is done by simple fractionation.

Refinery being a main energy source, has to avail as much less energy as possible during processing of crude. Bountiful combinations of heat exchanging systems were explored for effective and economic extraction of heat, the result of which a criti-

cally designed refinery consumes less than, 3 per cent of energy equivalent of crude processed. Destined to extract heat from different fractions before they reach storage, desalted crude is pumped through different heat exchangers arranged serially. The system is so effective that the temperature of the crude often reaches around 200°C , some reports say almost up to the topping temperature.

It is advisable to route part of the crude through exchangers and mingle with the rest of the crude, before it enters pipe still heater. The exchangers generally belongs to distillation columns, through which hot fraction exchange with crude.

Fig. 3.11 shows a two stage distillation unit. Crude after delydration and desalting is pumped through a number of heat exchangers. The preheated crude enters the furnace (1) to attain the topping temperature (normally 330 to 360°C). The hot crude is flashed in atmospheric column (2).

The distillation causes the fractions to separate in increasing order of boiling points. The top product being highly volatile has to be condensed in a reflux condenser. Some portion of the condensed fraction goes back as reflux. This fraction is rich in volatiles hence stabilisation of these fractions is done to obtain components like butane and pentane and depentanised gasolene.

All other fractions form the side draw products of distillation column. These fractions are precisely tailored in a side stream stripper (3). There shall be three to five side fractions depending upon the design. The fractions are usually classified as heavy naphtha, kerosene, diesel.

Bottom product of atmospheric column is now again routed through a furance to reach a temperature of 350 to 400°C and is allowed to flash in a vacuum column (4). Vacuum gasoil/heavy diesels, lube oil cuts/pressure distillates shall be the side cuts. The bottom product of vacuum column is known as goudron, and is meant for bitumen making or for coking.

Side stream strippers form usually a part of distillation column and their duty is to rectify the fractions to close approach of specifications. From these side stream strippers, the fractions pass through heat exchangers either for treatment or for storage. These are the exchangers which will supply the heat to crude.

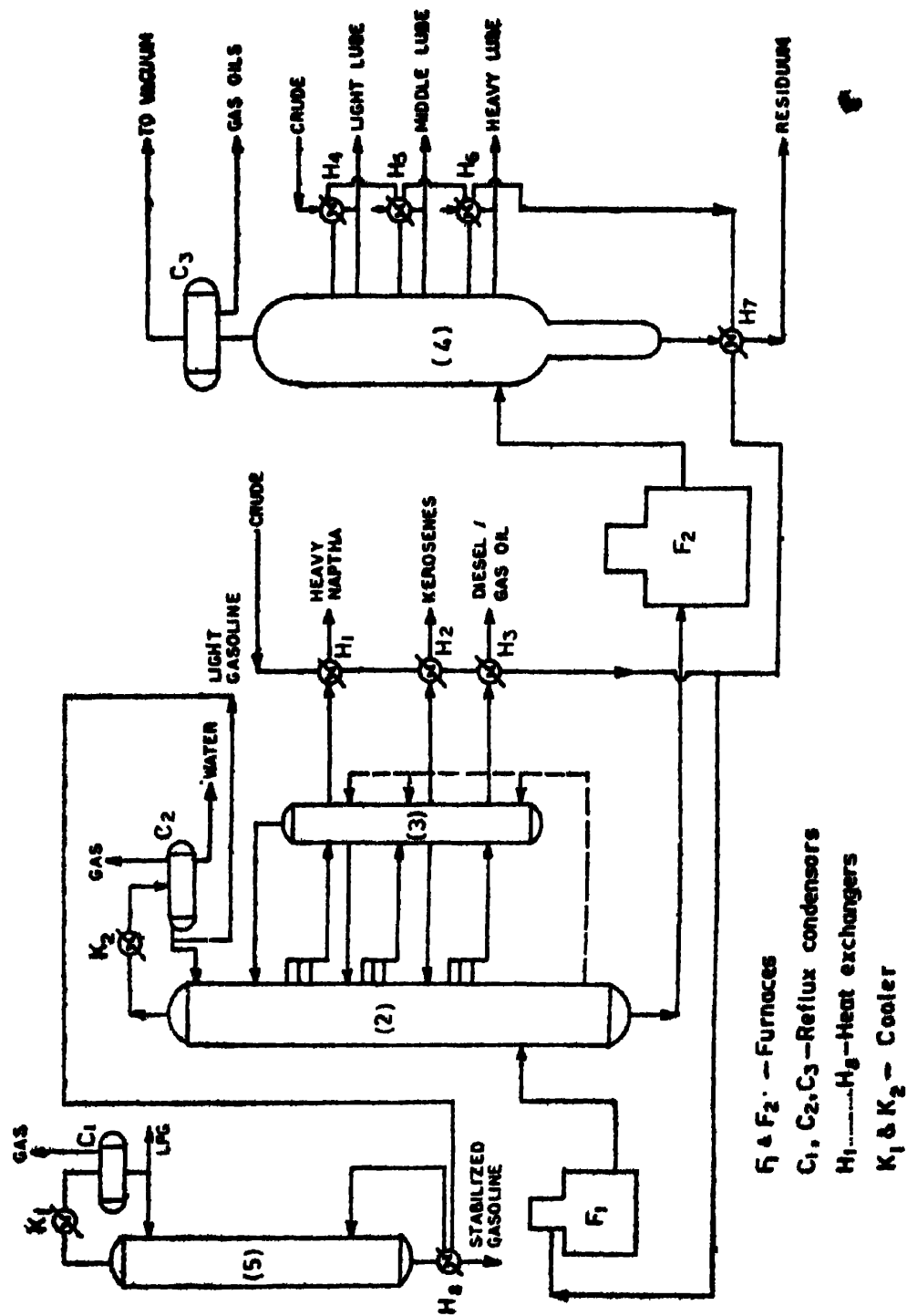


FIG. 3.11 Two stage Distillation Unit with Stabiliser.

Light fractions from the reflux condenser and first side cut fraction from ADC, shall constitute the main straight run gasoline fraction. This fraction is independently stabilised in a tall column (5), perhaps containing 40 to 50 plates.

Stabilisation is required to adjust ASTM distillation characteristics and RVP of gasoline. The top product from the stabiliser is a rich mixture of C_3 to C_4 fraction.

Butanes and pentanes generally are employed for blending in gasoline mixtures to guard the characteristics of light ends.

Stabilisation of crude is also common, specially when the crude contains huge amount of light ends. Storing and transportation of such crudes often pose problems, hence stabilisation is undertaken.

Naphthas (solvents) jet fuels, and other products are generally in the boiling range of gasolines to kerosenes and have to be separated either in a different unit or obtained as products by modifying side stream stripper operating conditions.

Problem 3.3

In a fractionation unit a light fraction, boiling range of 225 to 325°C, is to be separated from a high waxy distillate (405—425°C) using steam distillation technique. If the distillation temperature should not exceed 200°C, find the number of moles of steam required for equimolal mixture of this stock. Pressure of the system remains at 760 mm.

Data : (a) Vapour pressure of light component at

$$200^\circ\text{C} = 650 \text{ mm}$$

Vapour pressure of heavy component at

$$200^\circ\text{C} = 35 \text{ mm.}$$

(b) Mol.wt of light fraction = 225, $c_p = 0.47$

Mol.wt. of heavy fraction = 435, $c_p = 0.42$

Solution :

(i) Assuming steam does not condense and the mixture is at 200°C.

$$\frac{\text{No. of moles of steam}}{\text{No. of moles of light component}} = \frac{\pi - p}{p} = \frac{760 - 650}{650}$$

where, π = total pressure of the system

p = pure component vapour pressure

No. of moles of steam to distill light component

$$= \frac{110}{650} = 0.169$$

No. of moles of steam to distill heavy component

$$= \frac{760-35}{35} = 20.7 \text{ or } 375.6 \text{ kgs}$$

Steam condenses

At 200°C latent heat of steam = 769.5 (Kcal/Kgm)

Heat content of the mixture from a temperature of 30°C to 200°C

$$= m_1 c_{p1} dt_1 + m_2 c_{p2} dt_2$$

$$= ML; \text{ and } (dt_1 = dt_2)$$

$$= (225 \times 0.47 + 435 \times 0.42) (200 - 30) = M \times 769.5$$

M Kgs of steam = 63.7 per Kg mole of light and heavy component

So total steam requirement of $63.7 + 375.6 = 439.3$ Kgs.

Problem 3.4

In a flash vapourisation experiment of benzene-toluene of equal amount, is vapourised at 295 mm. pressure and 65°C temperature. Find the vapour composition. If the separation is conducted at 1300 mm. pressure and 110°C, find the composition.

Vapour pressures (m.m)

		65°C.	110°C.
Benzene	—	440	1850
Toluene	—	150	750

Solution

Mol.wt. of benzene = 78

Mol.wt. of toluene = 92

1st case

Moles of benzene in vapour = $\frac{440 \times 0.5}{295} = 74.6\%$ approx.

Moles of toluene in vapour = $\frac{150 \times 0.5}{295} = 25.4\%$

2nd case

$$\text{Moles of benzene in vapour} = \frac{1850 \times 0.5}{1300} = 71.2\%$$

$$\text{Moles of toluene in vapour} = \frac{750 \times 0.5}{1300} = 18.8\%$$

Problem 3.5

A distillation column is fed with feed at its bubble point. A reflux ratio of 4 is used. From the operating data given below, calculate number of plates, feed plate and its temperature required to obtain the following compositions :

DATA :

	Feed (moles) (F)	Overhead moles (D)	Bottoms (W)
Pentane	60	59.5	0.5
Hexane	20	0.5	19.5
Heptane	20	—	20.0
	100	60.0	40.0

Basis : Reflux ratio 4

Solution :

Mole fractions of these components in feed, overhead and bottoms :

	Feed	Overhead	Bottoms
Pentane A	0.6	0.992	0.012
Hexane B	0.20	0.008	0.488
Heptane C	0.20	—	0.500
	1.00	1.000	1.000

Operating lines

Below feed point : (Reflux ratio) = $L_n/D = 4$

Reflux = $4 \times \text{overhead} = 4 \times 60 = 240$ moles (LN)
product

$$\text{Total vapour} = 240 + 60 = 300 \quad (V_m)$$

$$\text{Liquid flow downwards : } L_n + F = 240 + 100 = 340 \text{ moles} \\ (L_m)$$

$$\text{Vapor } (V_m) : [(L_m - W)] 340 - 40 = 300$$

Operating lines for each component (below feed plate)

$$Y_m = L_m/V_m x_{m+1} - \frac{W}{V_m} x_w = \frac{340}{300} x_{m+1} - \frac{40}{300} x_w$$

Y_m stands for vapor composition corresponding to X_{m+1} .

$$\left. \begin{array}{l} \text{For } A : Y_A = 1.133 x_A - 0.134 \times 0.012 \\ B : Y_B = 1.133 x_B - 0.134 \times 0.488 \\ C : Y_C = 1.133 x_C - 0.134 \times 0.5 \end{array} \right\} \text{Set—I}$$

Above feed plate, the composition of vapor is given by,

$$Y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D}{V_n} x_D \quad (V_n = V_m)$$

$$\text{For } A : Y_A = \frac{240}{300} x_A + \frac{60}{300} x_D$$

$$\left. \begin{array}{l} A : Y_A = 0.8 x_A + 0.1984 \\ B : Y_B = 0.8 x_B + 0.0016 \\ C : Y_C = 0.8 x_C \end{array} \right\} \text{Set—II}$$

Starting from bottom composition, corresponding vapor composition is calculated. From the vapor composition using the Set-I eqns. for individual components the liquid composition in the above plate is calculated. This procedure continues till the feed plate composition is obtained. Above feed plate Set-II. eqns. are used to calculate the compositions.

It is understandable that the mixture should always boil between the BPs of high boiling component and low boiling component. At any temperature in between these limits, the equilibrium constants (K) for each of these fractions are found out and to match $\sum Kx = 1$. number of trials, for K are necessary.

TABLE 34

Component	X_w	K's at* 79.5°C	X_w	Y_w	X_{w-1}
A	0.012	3.3	0.0396	0.039	0.04
B	0.488	1.39	0.678	0.677	0.65
C	0.500	1.57	0.285	0.284	0.31
			1.0026	1.000	1.000

Y_w is corrected to $\Sigma Kx_w=1$; x_{w-1} is liquid composition in the above plate; obtained from eqn. of Set-I**

* Consult Chemical Engineer's Handbook, Perry.

** Elements of Fractional Distillation, Robinson and Gilliland.

$$Y_A = 1.133 x_A - 0.0016 \quad \therefore 0.039 = 1.133 x_A - 0.0016$$

$$\text{or } x_A = 0.04$$

	X_1	K at 72.3°C	$\Sigma KX_1=Y$	Y_1^*	X_2	K at 66.7°C	ΣKX_2	Y_2
A	0.04	2.8	0.112	0.111	0.099	2.5	0.2475	0.247
B	0.65	1.15	0.7475	0.744	0.715	0.95	0.6792	0.679
C	0.31	0.47	0.1457	0.145	0.186	0.40	0.0744	0.074
			1.0052	1.000	1.000		1.001	1.000

	X_3	K at 61.7°C	Y_3	X_4	K at 54°C	Y_4	X_5
A	0.219	2.0	0.438	0.388	1.66	0.645	0.571
B	0.657	0.8	0.525	0.520	0.64	0.333	0.351
C	0.124	0.3	0.037	0.092	0.24	0.022	0.078
			1.000	1.000		1.000	1.000

* Adjusted value for $\Sigma KX=1$

Feed-I Composition approximately matches fifth plate

	X_5	K at 46.6°C	Y_5	X_6	K at 41.7°C	Y_6	X_6
A	0.571	1.42	0.81	0.764	1.2	0.909	0.888
B	0.351	0.5	0.175	0.217	0.41	0.088	0.108
C	0.078	0.19	0.015	0.019	0.145	0.003	0.004
			1.000	1.000		1.000	1.000

	K at 38.4°C	Y_7	X_8	K at 38°C	Y_8	X_9	37°C
A	1.08	0.96	0.952	1.03	0.983	0.98	1.01
B	0.36	0.039	0.047	0.35	0.017	0.02	0.345
C	0.125	0.001	0.001	0.122	—	—	—
		1.000	1.000		1.000	1.000	

Y_9 composition is A 0.993 which is approximately equal to designed overhead composition

B 0.007

C —

1.000

Hence nine plates are required for this operation.

Feed plate is number 5.

Distillation temperature ranges from 79.5°C to 37°C.

Problem 3.6

A crude distillation is a column having a capacity of 10,000 bbls per day. Because of ineffective desalting the chloride (Cl^-) ion concentration at the top of the column is found to be 500 ppm. If the crude contains volatile sulfide (H_2S) upto 0.7 gms/liter. Find the amount of ammonia required for neutralisation. (One barrel is approximately 200 litres) A P I gravity of crude is 20.

Sol : 500 ppm Cl^- ion is equivalent

$$= \frac{500 \times 10000 \times 200}{1000 \times 1000}$$

$$= 10.0 \text{ kgs/day}$$

$$\text{H}_2\text{S content} = \frac{0.7 \times 1000 \times 200}{1000} = 1400 \text{ kgs/day}$$

$$\text{or } \frac{0.7 \text{ gm. moles}}{34 \text{ liter}}$$

P_H of the solution to be maintained at 6

System consists of $\text{H}_2\text{S} - \text{NH}_4\text{OH}$ ($\text{NH}_3 + \text{H}_2\text{O}$)

The first ionisation constant of H_2S at $25^\circ\text{C} = 9.81 \times 10^{-8}$

P_H of the buffer is given by equation

$$P_H = P_{K_a} + \log \frac{\text{salt}}{\text{Acid}}$$

where K_a is ionisation constant, Salt is ammonium hydrogen sulfide ; and Acid is H_2S .

$$\text{i.e. } 6 = -\log (9.81 \times 10^{-8}) + \log \left(\frac{\text{Salt}}{0.7/34} \right)$$

$$\log (\text{Salt}) = 6 + \log (9.81 \times 10^{-8}) + \log \left(\frac{0.7}{34} \right)$$

Salt equivalent to 68.6×10^{-3} kgs/day of ammonia, so total requirement of ammonia = ammonia required for chloride ion + 63.6

$$= \frac{10 \times 17}{35.5} + 68.6 \times 10^{-3}$$

$$= 5 \text{ kgs/day}$$

3.36 CALCULATION OF PLATE TEMPERATURES

It has been reported in the literature that the slope of a flash curve is practically independent of pressure. This makes easy for drawing flash curve at any pressure, once flash curve at a known pressure is available. Either the percentage intersection of T B P and flash curve or 50% boiling point of flash curve at that pressure be known available. The effect of diluent (steam) on the overhead product and its temperature (draw) could be better understood by the following illustration.

Problem 3.7

An atmospheric column is operating at 810 mm Hg. The top product light naphtha has a final boiling point of 140°C. Reflux on the top plate is maintained at 2.5 : 1. The condensate is found to contain 6 Kgs of water per every 100 Kgs of hydrocarbon. From this calculate the draw temperature of tray and partial pressure of hydrocarbon

(Assume Mol. wt. of HC as 130)

From this data it is understood that the 100% boiling point on flash curve is 140°C at normal pressure.

100 Kgs of HC

$$\begin{aligned}\text{Total product of HC} &= 1000 + 2.5 \times 1000 \\ &= 3500 \text{ Kgs}\end{aligned}$$

$$\text{Rates} = \frac{3500}{130} = 26.93$$

$$\text{Moles of steam : } \frac{.06 \times 3500}{18} = 11.67$$

$$\text{Total moles} = 38.60$$

$$\text{Partial pressure of HC} = \frac{26.93}{38.60} \times 810 = 565.2$$

At this pressure 100% EFV boiling point shall be (Fig. 2.4).
The draw temperature of the plate = 126.5°C

In commercial operations, the draw temperatures, are found to be slightly less than the calculated ones for middle distillates where the effect of steam is not commendable. Draw temperatures are approximates taken as

$$0.88 \times (5\% \text{ point on TBP cut})$$

The sound method of calculating the temperatures at the draw plate is by heat balance in that section ; however this is also a complex thing.

3.4 BLENDING OF GASOLINES

Blending, an important operation in refinery, is a physical process in which accurately weighed quantities of two or more components are mixed thoroughly to form a homogenous phase ; the components mixed being similar or dissimilar in nature.

Most of the products obtained from distillation columns are invariably blended with fractions obtained from other units to help in keeping the wastage minimum and increasing the quantitative production. Almost all products from gas to lube oil are not only blends of fractions but additives too. All such blends shall be formulated to have the required properties conforming to the specifications.

3.4.1 BLENDING PROCESSES⁴¹

There are two ways by which effective blend can be produced; one is by batch blending the other is continuous blending. Batch blending starts with mixing known amounts of components in a tank mixer. The mixer shall be fitted with an agitator and other accessories like pressure gauge, liquid level indicators etc. Sometimes agitation by blowing air is convenient. Suction blending is quite alluring specially when toxic materials like lead, biocides are blended. Mixing in tanks furnishes some advantages like inserting cooling or heating coils in tanks.

3.4.1.1 *Line Blending*

This is widely used in refineries as well as in blending plants. All components to be blended are pumped simultaneously into a common header at rates specified as per the formulations (Fig. 3.12). Rate of flow is proportioned by control valves operated by pneumatic or electric relay system. Signals received are corresponding to flow rates, and these can accurately modulate the flow rates by adjusting valve openings.

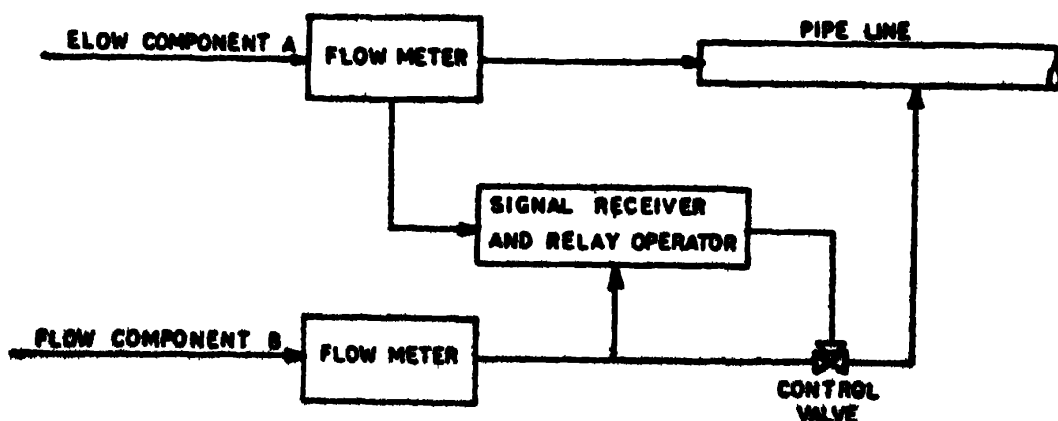


FIG. 3.12 Schematic Diagram for Blending Gasolines

The long pipe line through which all these proportioned components travel acts as a mixer to produce the blend. Additives can also be injected into the system.

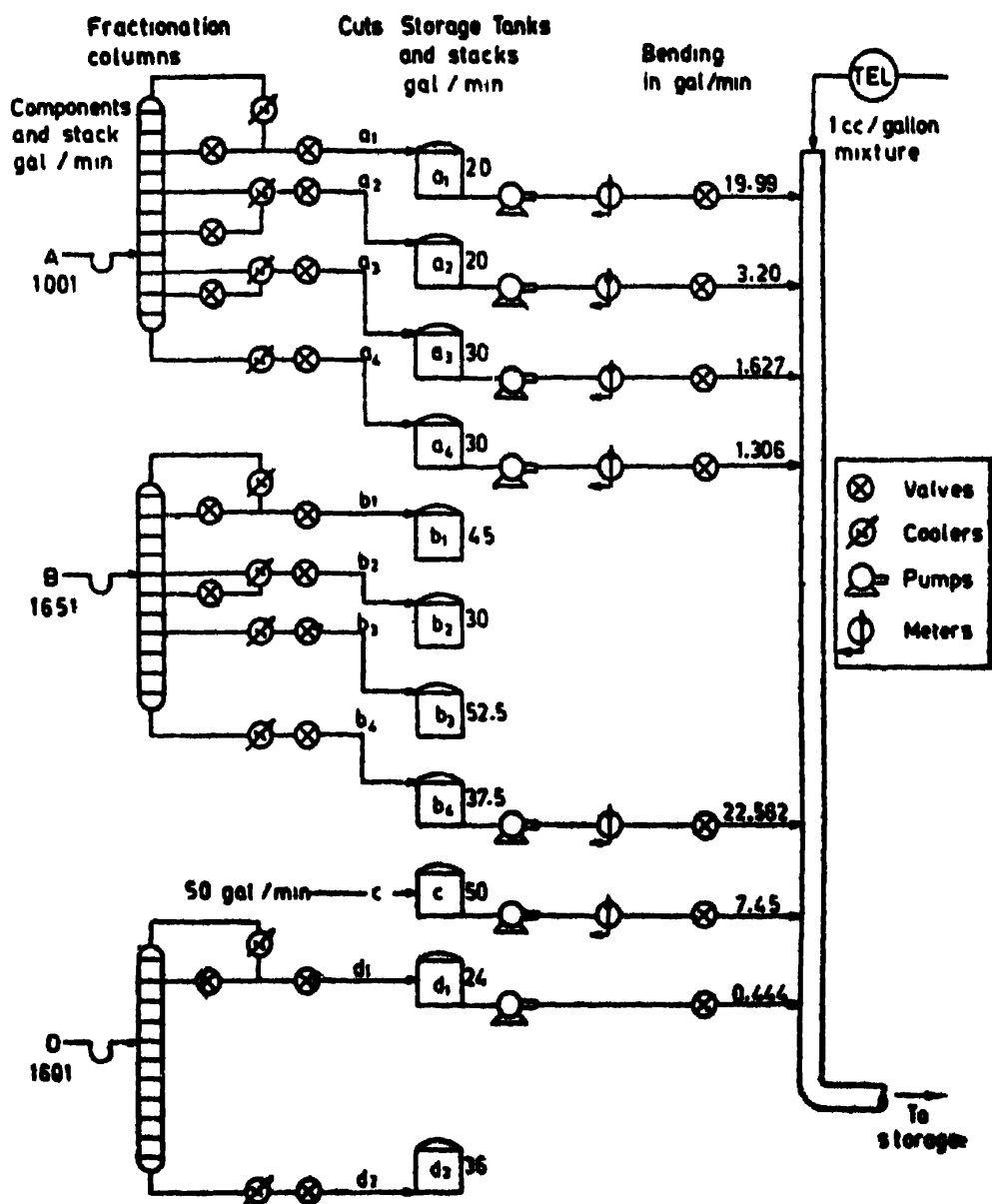


FIG. 3.13 Pipe line Blending of Gasoline

TABLE 35

DATA OF COMPONENTS

Component	B P °C	at 15°C sp gr	Mol wt	O N.	Component cuts	B P. °C	Sp gr at 15°C	Mol. wt	Octane No	Vapor pressure (mm) 37.8°C
A	35—180	0.7133	99	61	a ₁	35—50	0.6521	75	70	720
B	65—200	0.8118	113	60	a ₂	51—75	0.6833	86	40	380
C	120—150	0.7846	125	95	a ₃	76—110	0.7188	100	70	160
D	78—180	0.7870	106	84	a ₄	111—180	0.7686	130	60	35
					b ₁	65—75	0.6845	90	40	300
					b ₂	76—110	0.7175	100	70	150
					b ₃	111—180	0.7666	125	60	32
					b ₄	180	0.7784	150	50	4
					d ₁	75—110	0.7844	90	90	160
					d ₂	111—180	0.7904	120	80	35

A = Straight Run

B = Straight Run

C = Alkylated stock

D = Reformed stock

TABLE 3.6
SPECIFICATION OF FINISHED PRODUCT

Temperature	% distillation
60°C	10 IBP. 42°C
115°C	50
175°C	90
Octane No (Research)	Minimum 65
R.V.P.	0.7 Kgs/Cm ²

3.4.1.2 Gasoline Blending

Different gasolines like alkylated, reformed polymer, cracked, straight run etc. are blended along with various additives to boost the performance value of gasoline; however the blend should faithfully respond to the specifications. The two important inviolable properties on which blends are critically constituted are vapour pressure and octane number.

Vapour pressure of a mixture can be estimated by Raoult's Law. But scant information on the molecular composition of a blend does not permit it; and laborious experimentation for evaluating molecular composition is also not wise.

The following problem on blending of gasoline exposes the labour involved in such blending operations.

Problem 3.8

In a refinery, the following gasolines are available. It is desirable to make a blend with these, guarding R V P and octane number as specified. Formulate the blend

Solution

A suitable blend has to be tried by trial and error methods. An initial blend composition is chosen arbitrarily that nearly satisfies octane number and RVP. The equilibrium composition of liquid and vapour are theoretically found out from equilibrium constants (K) at a particular temperature. As shown in specifications, 10% of the stock has to be distilled at 60°C. The problem is to first find out the equilibrium composition of liquid with

TABLE 3.7
BLEND-COMPOSITION-PROPERTIES

Feed X_1 mol. fraction	Vol of feed X_1 (cc)	K at 60°C	$V/L = \frac{.13}{.87}$ X_A	$X_F =$ 0.87 X_A	Vol. 0.87 X_A	K at 115°C	$V/L = \frac{.58}{.42}$ X_A	0.42 X_A	Vol. 0.42 X_A	
a ₁ :	0.45	51.75	2.10	0.3937	0.3425	39.38	7.20	0.0979	0.0411	4.73
a ₂ :	0.066	8.30	1.00	0.0660	0.0574	7.23	4.50	0.0217	0.0091	1.15
a ₃ :	0.030	4.21	0.60	0.0316	0.0274	3.85	2.70	0.0151	0.0063	0.89
a ₄ :	0.020	3.38	0.10	0.0226	0.0197	3.33	0.37	0.0315	0.0132	2.23
b ₄ :	0.303	58.38	0.01	0.3477	0.3025	58.29	0.095	0.6377	0.2678	51.68
c :	0.121	19.48	0.10	0.1370	0.1192	19.19	0.41	0.1839	0.0772	12.43
d ₁ :	0.01	1.15	0.60	0.0105	0.0092	1.05	2.7	0.0050	0.0021	0.24
Total :	1.00	146.65		1.0091		132.32		0.9928		73.35
Distilla- tion %						9.8%				49.98%

TABLE 3.7 (Contd)

BLEND-COMPOSITION PROPERTIES

K at 175°C V/L = $\frac{0.92}{0.08}$	$X_A = \frac{X_A}{0.87X_A}$		Vol. feed	R.V.P. of the feed (mm)	Octane number of the feed
	X_A	$0.87X_A$	$0.08X_A$		
16.0	0.0304	0.0024	0.28	324	0.45 X 70
12.0	0.0059	0.0004	0.06	25.08	0.066 X 40
5.8	0.0055	0.0004	0.06	4.8	0.030 X 70
0.95	0.0209	0.0016	0.28	0.7	0.020 X 60
0.31	0.8296	0.0663	12.79	1.20	0.303 X 50
1.40	0.0884	0.0070	1.13	4.23	0.121 X 95
5.8	0.0018	0.0001	0.02	1.6	
Total	0.9825		14.62	361.6	0.01 X 90
Vol %			90.04 %	0.7 Kgs/cm ²	64+1CC TEL/gallon

vapour, at that temperature for 10% distillation ; the molar ratio of vapour to liquid is found to be 0.13/0.87. Now finding the K values for these components which depend upon the vapour pressures, the vapour composition is found out.

Say in the case of straight run gasoline a fraction 35 to 50°C is named as component (α_1), has an equilibrium constant 2.1 at 60°C. Assuming a feed composition 0.45 mole fraction in the mixture, its vapour composition⁴⁸ is given by

$$X_A = \frac{X_{AF}}{L + (1-L)K}; \quad P_A/P = K$$

Where = X_A : Eq. concentration of A with vapour.

X_{AF} : 0.45

X_B : Residual liquid composition at 60°C.

L : Fraction of liquid residual.

$P_A/P =$: K

P_A : Vapour pressure.

P : Total pressure (760 mm)

$$X_A = \frac{0.45}{2.1 \times 0.13 + 0.87} = 0.3937.$$

Like this for all components⁴⁸ the residual liquid composition (X_B) is found at

i.e. $0.3937 \times 0.87 = 0.3425$

for all components $\alpha_1, \alpha_2, \alpha_3, \alpha_4, b_4, c$ are found out when $X_B = 1$. Otherwise the calculations are repeated choosing the different compositions of the feed mixture. The volume of the portion distilled is found out by knowing the density and mole fraction of the individual component in condensed vapour, which is very nearly equal to 10% of the distillation. In the same way the calculations are repeated at different temperatures 115°C & 175°C and corresponding percentage amounts of distillates are found out. The RVP of the final mixture, satisfying the distillation pattern is thus evaluated. The blend may slightly differ in octane number, and it is to be boosted by lead as shown in Table 3.7. & Fig. 3.13.

Generally refiners depend upon two components butane and pentane as the vapour pressure adjusters. For easy estimations depentanised gasoline shall be regarded as low volatile component, whose vapour pressure is more or less constant at given tempera-

ture. By adding highly volatile butanes of known amounts the vapour pressure can be easily adjusted. In practice blending values are assigned to each component and the value for butane is taken as 100. With respect to butane other components are assigned the blending values depending upon the volatility. The vapour of the mixture can be derived by law of additives.

Problem 3.9

Different gasolines are to be blended along with n-butane. Find the resulting vapour pressure of blend from the data given below :

	Blending Value at 38°C	Volume % in blend
Alkylated gasoline	5.0	10
Cat. cracked gasoline	27.3	20
Straight run gasoline	30.	60
n-butane	100	10

Solution :—

Contributed value of each fraction

$$\text{Alkylated gasoline : } \frac{5 \times 10}{100} = 0.5$$

$$\text{Cat. cracked gasoline} = 27.3 \times \frac{20}{100} = 5.46$$

$$\text{Straight run gasoline} = 30 \times \frac{60}{100} = 18.0$$

$$\text{n-butane} = 100 \times \frac{10}{100} = 10.0$$

Total value of blend : 23.96

Octane value of a blend follows strictly the additive principle (by volume) ; hence a marginal adjustment may be tried with TEL or TML when ever a blend falls short of the value two to three units.

3.4.2 INTEGRATED REFINERIES

Present trend is to install a refinery at the consumer point rather than at the place of oil production. This can harvest the riches to a great extent, as the products are immediately sold, thus

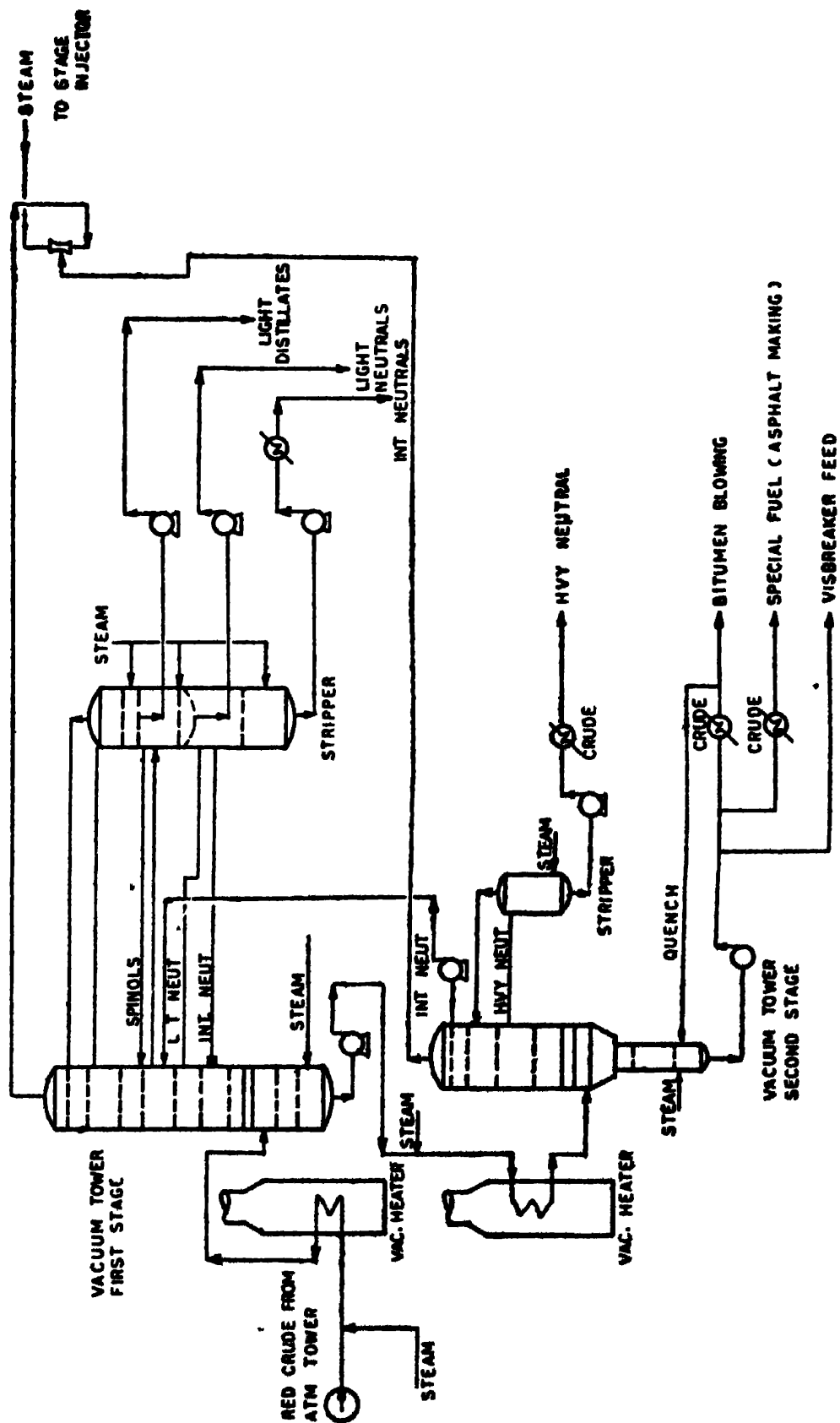


Fig. 3.14 Lay out of a modern Petroleum Refinery (contd.)

not much with holding of investment. Further, the basic petrochemical industries expedient for other necessities can be instituted. The modern refinery gingerly incorporates on an intergrated circuit, all necessary treatments, waste disposals storage facilities etc. A modern refinery lay out is shown in Fig. 3.14. ,

Modern refinery is a much cleaner industry compared to many other industries. However, even if a low sulfur crude is handled the off gases containing sulfur, shall be high. For example a 3 million ton plant processing 0.10% sulfur crude can easily give rise to pollution problems (as the off gas contains roughly 30% of sulfur intake). The tendency, of recovering sulfur is increasing, as it forms a cheap by product, specially for a country like ours.

Disposal of acid sludges, clays, water, gas etc. all require prudent planning.

Fire hazards though uncommon, cannot be overruled. Fire fighting equipment should be in the reach of all units.

Most of the refineries in our country, like elsewhere, are coastal based; this helps in an unfaltering way the disposal operations.

PROBLEMS

1. (a) A petroleum stock at a rate of 1200 bbl/hr. (sp. gr. 0.8524) is passed through heat exchangers before it is fed into radiant section of a box type heater at 200°C. The pipe still heater burns refinery off gas at a rate of 3,250 kgs/hr. The refinery off gas has a heating value of 11,300 Kcals/kg. In the radiant section of furnace, there is one row of tubes of 12 metres long of 10.5 cm. O.D. spaced at 2 ; O.D. The projected area of tubes is 150 sq. metres.

Find the outlet temperature of oil

(Air fuel ratio 25)

Sp. heat 2.66 kJ/kg°C

(Ans. 342°C)

(b) Find the volume of the furnace (combustion space only). Comment on the heat density in this furnace as well as heat generation capacity with respect to projected area of tubes.

Ans. 560 cubic meters.

(c) Calculate the area of duct. Assume a reasonable mass flow rate of gases.

2. A petroleum stock at a rate of 1000 bbl/hr. is passed through convection section of box type heater. In this process the temperature of the feed is raised from 30°C to 180°C. Assuming an average flue gas velocity 2 meters per sec. at an average temperature of 625°C. Find the heating area required.

Data :—

O.D. of the tube 10.05 cm.

Mass flow rate of gases 100 kg/sec. sq. meter.

Sp. heat of stock : 0.52 kgcals/kg.°C.

3. Carbontetrachloride to be steam distilled. The ambient pressure is 775 mm Hg. Calculate how many K. Cals are required to distill 100 kgs. of CCl_4 , starting with a mixture of 50 kgs of water and 500 kgs of CCl_4 at a temperature of 25°C.

(Use Cox chart to get the boiling point of this mixture try between 65°C-68°C).

Latent heat of vaporisation of CCl_4 : 46.5 gm. Cals/gm.

(Ans. 13504 kg cals)

4. The vapour pressures for Toluene and Benzene are given below at different temperatures. Assuming that mixture obeys Raoult's Law construct the B.P. diagram at 760 mm Hg total pressure and compare it with 900 mm Hg total pressure.

Problem 4 : (Data)

T°C	Vapour Pressures	
	Benzene (A)	Toluene (B)
80	760	—
82.2	811	314
87.7	957	378
93.3	1123	452
99.0	1310	538
107.2	1520	635
109.2	1620	687
112.0	—	760

5. A Butane-pentane mixture containing 40% butane is distilled at 90°C at 10 Kg/cm² pressure. Find the composition of condensate.

Equilibrium vaporisation constant

for butane	1.32
for Pentane	1.32

(Ans. 0.82 Butane
0.18 Pentane)

6. A 2 mt refinery distills crude that contains chlorides and sulfur to an extent of 700 ppm and 2000 ppm respectively. If PH at the top of the column is maintained at 6 ; to avoid corrosion—(a) find out the requirement of ammonia,

(b) Blend of naphtha from the same refinery has the following overhead composition (in stabiliser). Suggest the methods for prevention of corrosion in stabiliser.

NO=10 ppm ; SO₂=50 ppm ; H₂S=0.001%
Other sulfur 0.0003%

Compounds

Chloride concentration=100 ppm.

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CHAPTER 5

Thermal and Catalytical Processes

5.1 Cracking

Dissociation of high molecular weight hydrocarbons into smaller fragments through agency of heat alone is termed as thermal cracking or pyrolysis. Cracking can also be conducted in presence of catalysts, and this has been differentiated from the former one by adding 'catalyst' term before cracking i.e. catalytic cracking. In either of these operations, the reactions widely follow the same lines yielding more or less similar products, however the course of reactions is explained by a different mechanism. Necessity of cracking operations has become a reality in refinery operations to augment the market demands by converting less valued fractions or unwanted fractions to more commercially valued products.

Developed countries like USA, convert more than 70% of crude by thermal processes or other techniques to motor spirit, while a developing country like ours has scant demand for gasolines though imposing demands for middle distillates exist. Thus thermal cracking operations are warranted in every country though not to same extent or for the same fraction at all times.

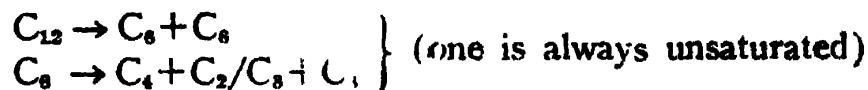
5.1.1 THERMAL CRACKING REACTIONS

Heat sensitive, high molecular weight paraffins fragment when temperature exceeds 400°C. A molecule of C_nH_{2n+2} ; where 'n' ranges from and above 25, easily splits into two, almost at the middle, resulting in one saturated molecule and other unsaturated molecule.

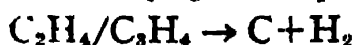
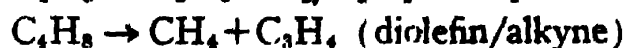


The above reaction is foremost and conclusive at moderate temperatures around 400°C, but fragmentation continues with increas-

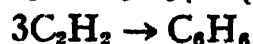
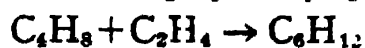
ing temperature, giving rise to often simple products and occasionally complex molecules. Appearance of different intrinsic reactions is common, depending upon the molecular size. For a paraffin of less molecular order, the following reactions illustrate the mode of cracking.



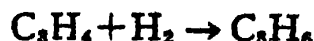
Unsaturates (olefins) obtained in the process crack again



Olefin cracks or dehydrogenates to diolefin or an alkyne. Further severity in conditions results in production of methane, hydrogen and carbon. These are regarded as stable and end products of cracking operations. Unsaturates being active under congenial thermal cracking conditions form dimers, trimers, etc. i.e. condensation to bigger molecules.

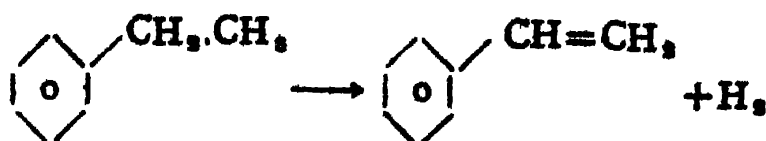
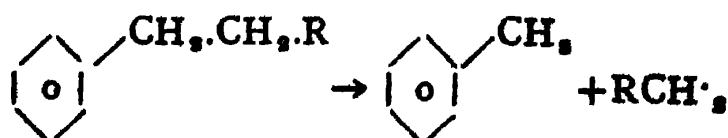


Hydrogenation also occurs but to a less extent

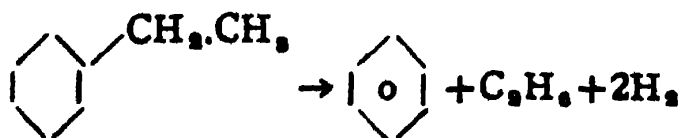


Aromatics, saturated ring structures follow a different pattern of cracking.

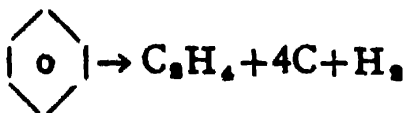
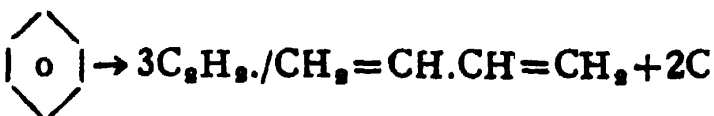
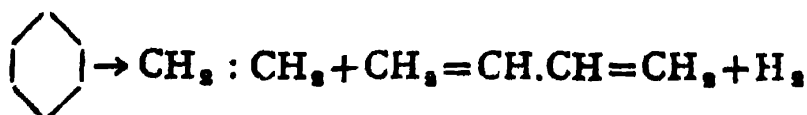
Chain detachment is frequent followed by dehydrogenation as shown below :



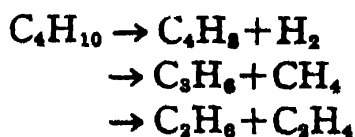
Saturates are converted to unsaturates



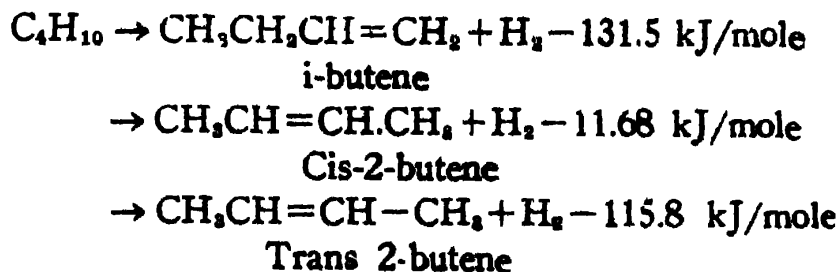
Ring opens in the extreme conditions of cracking



Above reactions illustrate carbon and hydrogen formation. Light paraffins when subjected to cracking de-hydrogenation reaction shall be imminent and it dominates over other cracking reactions :



The tendency of dehydrogenation becomes less, where the chosen molecule is above C_4 . Dehydrogenated molecule normally exhibits isomeric forms, such as



A plausible explanation based on all these reactions concedes that the product of cracking may have higher-molecular weight than the feed itself, obviously due to polymerisation or condensation

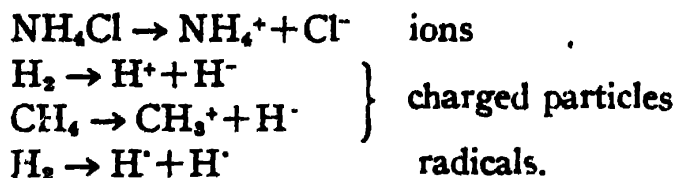
Martin and² Will enlisted information on cracking severity and its innate spectrum of products : the information in Table 5.1 is based on it.

5.1.1.1 Theory of Thermal Cracking

Cracking proceeds via free radical mechanism. Free radicals are atoms or group of atoms with bare unpaired electrons, thus differing from other types of charged particles known as ions. The following reactions explain the difference.

TABLE 5.1
THERMAL CRACKING OPERATIONS

Cracking temperature °C	Nature of operation	Products
425—460	Visbreaking	Fuel oil
460—520	Thermal craking	Gas, Gasoline. Tar oils, Circulating oils.
520—600	Low temp coking	Gas, gasoline soft coke,
600—800	Gas production	Gas and unsaturated
800—1000	High temp coking	Gas, heavy aromatics pitch or coke
above 1000	Decomposition	H ₂ , gas, carbon-black



In a molecule of hydrogen there are two electrons sharing the spin in opposite directions.

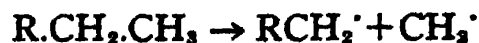
For hydrogen paired electrons are arranged in S-shell like



. When atomic hydrogen is formed without charges unpaired electrons result in S-shell : H₂ →



Similarly



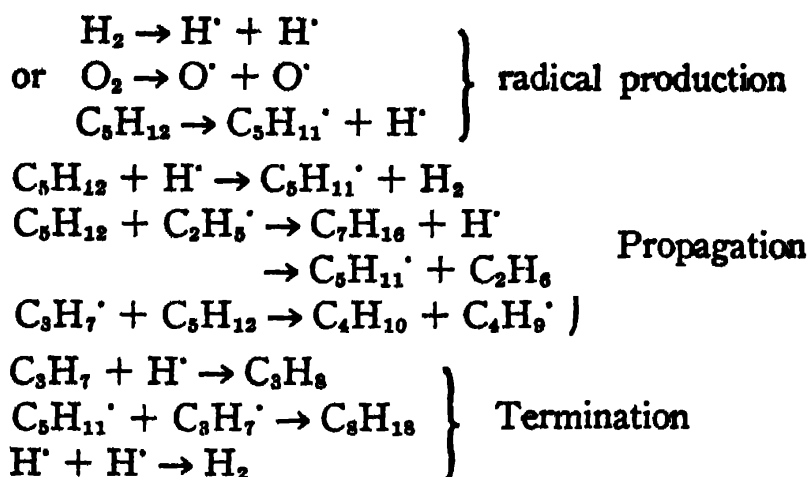
These unpaired electrons are very active, and try to form stable compound by acquiring unpaired electrons from sources available. Motive power of free radicals to combine with other radicals or

metallic bodies is immense; generous dissociation into small radicals is also high.

Hydrocarbon (charged) ions are usually referred as carbonium ions or carbanion ions depending upon the charge they carry.



The reactions of free radicals are fast; indeed only one radical is sufficient to bring about a series of reactions as shown below :



Different free radicals have different lives. Hydrogen free radicals have the highest stability and so a higher life. The stability or life of a radical decreases with the increasing size of molecule. Minimum bond energies invoke the scission at a convenient position during the reactions. The bond energy of C-C is 262.7 kJ/mole while C-H bond requires 358 kJ/mole to break open. Some of the bond energies given by different authors is furnished below^a :

Bond	Energy kJ/mole			
	Author	Polanyi	Stevenson	Kistiakowsky
CH ₃ -H		428.76	422.90	426.67
C ₂ H ₅ -H		407.84	404.91	409.93
n-C ₃ H ₇ -H		397.39	414.12	—
i-C ₃ H ₇ -H		372.29	391.11	—
CH ₃ -CH ₃		363.92	348.86	358.06
CH ₃ -C ₂ H ₅		355.56	339.24	350.54
C ₂ H ₅ -C ₂ H ₅		—	330.46	344.68

Due to the high stability of tertiary carbonium ions, the asymmetric carbon bonds are easily ruptured than the symmetrical ones. This is amply sufficient to explain why isomerisation does not result in thermal cracking operations. The free radical mechanism offered by Rice, though it cannot correctly predict the composition in kind and quantity of the products, still, is the best tool in view of the complexity of reactions.

5.1.1.2 *Properties of cracked materials*

Product properties are extensively dependant on the conditions of cracking. A cracked product acquires refractory nature, and hence severe conditions are required for cracking such stocks (these are also known as recycle stocks). For smooth operations a fraction of cracked stock (high molecular weight) is mixed with the incoming charge and cracked. Evidently the properties that undergo changes during cracking are

- (a) Characterisation factor (decreases)
- (b) Boiling point, viscosity, pour point (decrease)
- (c) Unsaturation and aromatisation (increase)
- (d) Octane number of gasoline (increases) and
- (e) Sulfur in cracked products increase as a rule, although the maximum amount is found in heavier portions only.

Cracking being endothermic, external heat is required. Cracking is preferentially conducted to obtain the desired products as closely as possible. Because of the complexity of reactions theoretical predictions may not be convincing. Best way to produce more of the desired low volatile fractions is by cracking the intermediates obtained in the operation.

Pressure, temperature and time are the main parameters which govern the cracking operations. At a given pressure and temperature the yield of light fractions is a function of time. Time of cracking, at a set conditions of temperature and pressure, increases with increase in API gravity of the feed. This explains why that heavier fractions crack easily. Yet at times the operation becomes extravagant due to high gas production. Deposition of coke checks the run lengths too. Thus the parsimony of the process is guided by gas and coke yields.

In an operation of a high crack per pass with low recycle ratio of intermediates, the resulting gasoline exhibits low and better volatility and high octane number. The effect of pressure on production of gas at different cracking rates is given in Table 5.2.

TABLE 5.2
EFFECT OF PRESSURE ON CRACKING

Gasoline conversion per pass	Gas (M ^a bbl) yield		
	Pressure		
	6.6 atms	13.5 atms	27 atms
10%	3.3	1.6	1.2
20%	8.0	4.1	3.5
30%	14	8.3	6.5

With increase in yield per pass the heat of decomposition also decreases. This is due to the increase in yield of gasoline. Proportional increase in yield to heat input is much higher. So at an yield of 30% gasoline the heat of decomposition is 1600-1700 kJ per kilogram. Yield of gasoline versus heat of decomposition is shown in Table 5.3.

TABLE 5.3
YIELD OF GASOLINE AND HEAT OF DECOMPOSITION

At a set of conditions of operation

Yield of gasoline	Heat of decomposition; kJ/kg
5%	5585
10%	3595
15%	2492
20%	1860
25%	1777
30%	1672

Summing up all the facts :

- (1) Pressure for all practical purposes has no direct effect on velocity of reaction. If more gases were to be produced then low pressures are desirable. With high pressures, gas to gasoline ratio becomes less.
- (2) Reaction velocity is directly dependent upon temperature only.
- (3) Recycling increases refractory nature of stocks, and hence, recycling should not exceed 2 to 3 times of fresh stock for economic operations

5.1.1.3 *Effect of pressure on cracking*

Obviously pressure retards cracking reactions. But in practice a positive pressure of 10 to 15 kgs/cm² is enclamped to minimise coke formation. Increase of pressure, decreases the yield of light fractions but in the earlier stages it may be quite favourable for production of diesels or circulating oils. Even though the decrease in heavier fraction may be anticipated the fall may not be so sharp.

5.1.1.4 *Depth of cracking and soaking factor*

In the initial stages of cracking, partially the concentration of feed stock remains unchanged. But with progress in cracking, mixed products result; naturally product concentration shall be different. To express the conversion in a better way, terms like severity or depth and soaking factor are introduced. Severity is mainly connected with temperature. Soaking factor on the other hand is connected with temperature and volume of feed per unit time. These two can furnish a lot of information on cracking operations; and may percept the operations too. Soaking factor is a comparative term, i.e. comparison is done by bringing the conditions of operation to some known conditions (Standard). The specified conditions for such comparison are : temperature 426.7°C and pressure 52.7 kg/cm². The soaking factor may be now defined as

$$SF = \int_0^v R \frac{K_T}{K_{426.7}} \frac{dv}{F}$$

where

R : constant, correction factor when operating⁴ pressure differs from 52.7 kg/cm².

$K_T/K_{420.7}$: Relative cracking reaction velocity at any temperature (T).

$\frac{dv}{F}$: Differential coil volume in liters per bbl of feed stock daily through put.

The above equation is suitable for vapour phase cracking only.

Rate of Reaction

Cracking reactions are described as first order reactions, when crack per pass does not exceed 25%. Rate is given by

$$K_t = \frac{1}{t} \ln \frac{a}{a-x}$$

where

t in seconds

a % of material in feed

x % of material that disappears in time t .

For a feed stock which does not contain any cracked product ' a ' becomes equal to 100. Frequently x is expressed in moles or by volume. When gaseous feed stocks are handled x is presented in moles, otherwise in volume only.

Temperature and reaction rate-constant are related by Arrhenius equation given below :

$$\ln K = -\frac{E}{RT} + C$$

where

$R = 8.3143$

$T = ^\circ K$

E = Energy of activation, kJ

C = Constant

E and C in the above equation are usually obtained from investigations. Such investigations are plenty in the literature.

Keith, Ward and Rubin, reported, after extensive studies, activation energy for gas oils as $-239 kJ$ and ' C ' as 31.924. Genisse and Reuter's⁵ values are slightly different and given as

–224 kJ and –28.8 respectively. Approximate values given by Nelson^{a,b} as $E = -227.9$ & $C = -30$, would be accurate enough for all theoretical considerations.

Heat of decomposition

It is not descretly possibly to ascertain the accompanying heat changes in the cracking reactions due to the complexities involved in bond ruptures and formations. Heat^{a-a} of cracking can be calculated by knowing molecular weights of charge stock and products. Such simplifications are amply available; as an example, an equation of immense help is presented below :

$$\text{Heat of cracking (kJ/gm)} = \frac{C(M_c - M_p)}{M_c M_p}$$

where

$$C = -1150.20$$

M_c/M_p , mole weights of charge and products.

The best method of finding out heat of decomposition is from the principles of conservation of energy i.e. heat of combustion.
Heat of decomposition = (Heat of combustion of products) —
(Heat of combustion of feed stock).

Problem 5.1

A thermal cracking operation of heavy gas oil has given rise to the products as given below.

(a) Find out the heat of decomposition per kg gasoline.

Data : Feed °API–37

Temp. of cracking–450°C

B.P. of feed .330–380°C.

Products :

Gases—12.3% average calorific value at 30°C

10.16×10³ kJ/kg.

Gasoline—30.6%, 68 °API, 44.22×10³ kJ/kg.

(Cal. Value)

Residuum—15% ; 15 API ; 35.53×10³ kJ/kg.

(Cal. Value)

Losses—2%

Uncracked feed—40.1% ; 41.8 kJ/kg. (Cal. Value)

(balance)

Basis 100 kg of heavy gas oil

Constituent	°API	Amount (Kgs)	Heat of combustion at 30°C (kJ/kg) ($\times 10^3$)	Total Heat content kJ ($\times 10^3$)
Gases	—	12.3	50.16	622.38
Gasoline	68	30.6	44.22	1,353.13
Residues	15	15.0	35.53	532.95
Losses	—	2.0	—	—
Remaining stock	37	40.1	41.80	—
Total heat content of products				2,508.46

Heat content of feed (including losses)

$$(100 - 42.1) (41.8) 10^3 = 2,420.22 \times 10^3$$

$$\begin{aligned} \text{Heat of dissociation} &= (2,508.46 - 2,420.22) 10^3 \\ &= 88.24 \times 10^3 \text{ kJ/kg} \end{aligned}$$

$$\text{Per Kg gasoline} = \frac{88.24 \times 10^3}{30.6} = \frac{2.556 \times 10^3}{1} \text{ kJ/kg.}$$

(b) If the cracking is conducted for 28 min. at 450°C, find the reaction constant and activation energy.

Assuming $C = 30$

$$\ln K_1 = -\frac{E}{RT} + C$$

$$K_1 = \frac{1}{t} \ln \frac{100}{100-x} \quad \text{where } x = 30.6 \text{ gasoline produced.}$$

$$= \frac{1}{1680} \ln \frac{100}{100-30.6} = 2.174 \times 10^{-4} \text{ sec.}$$

Substituting for K_1 in the equation

$$R = 8.3143$$

$$T = 723^\circ K \text{ \& } C = 30$$

$$\text{Activation energy, } E = 230.726 \times 10^3$$

5.1.2 VISBREAKING

In the wide spectrum of thermal cracking operations (Table 5.1), visual observations reveal visbreaking is the inci-

cient stage. Its name significantly exposes that there is reduction of viscosity during this operation. Materials like residuums of not direct utility or stocks besieged with difficulties due to high pour point, form the palapable feed stocks for this operation. The liquid products may be used as good cycle stocks for catalytic crackers although the commercially valuable main product is listed as fuel oil ; light fractions like gas and gasoline invariably accompany in all the cracking operations.

5.1.2.1 Visbreaking operation and description

Fig. 5.1 shows the operation. Feed stock comprising variety of materials ranging from asphalts, short residuums to medium oils is blended separately and passed through heat exchanging system (1) : the temperature rise in such exchanger is close to 250°C . The preheated stock, is heated in a furnace (2) to attain a temperature of 470°C . A pressure of 10-15 kg/cm^2 is essential to keep the coke forming reactions in dormant state. Obliging steam admission into feed stock checks coke formation, thereupon

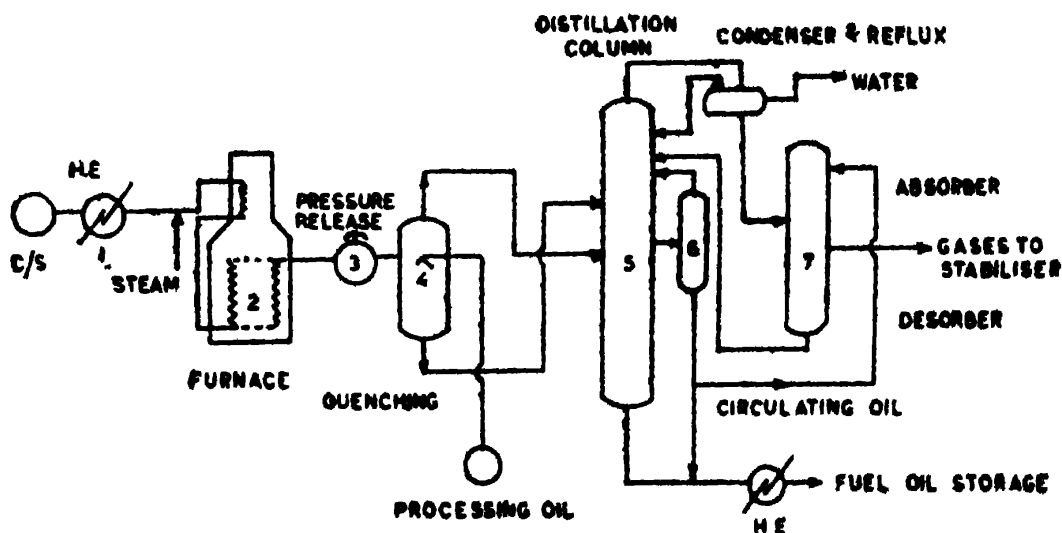


FIG 5.1 Visbreaking

the life of tubes can be increased. The cracked products pass through a pressure releasing valve (3) only to be quenched in a quencher (4) effectively with processed heavy oils. The light fractions and bottom fraction from this quencher go into a dis-

tillation column (5). At the top of column, the condenser system separates water and supplies adequate light fraction reflux to column. These light fractions with gases are sent to an extractor (7) to absorb gases. The top portion of the extractor is meant to dissolve gasoline like fractions in circulating oils, and the bottom section of the extractor acts a stripper to free the gases. The circulating oil with dissolved fraction is again sent back to the distillation column (5). From the side stripper (6) the circulating oil is tapped as a bottom product, part of which is mixed with the bottoms of column (5) and sent to storage system through process heat exchangers. The addition of circulating oil to fuel oil maintains the required plasticity. Gases from stripper are sent to gasoline stabilizer for recovering butane and the rest are sent to gas stream circuit of refinery.

5.1.2.2 *Operating conditions and products*

Operating data on visbreaking of Nahorkatiya⁶ long residuums are furnished in Figs. 5.2a & b. With increase of crack-

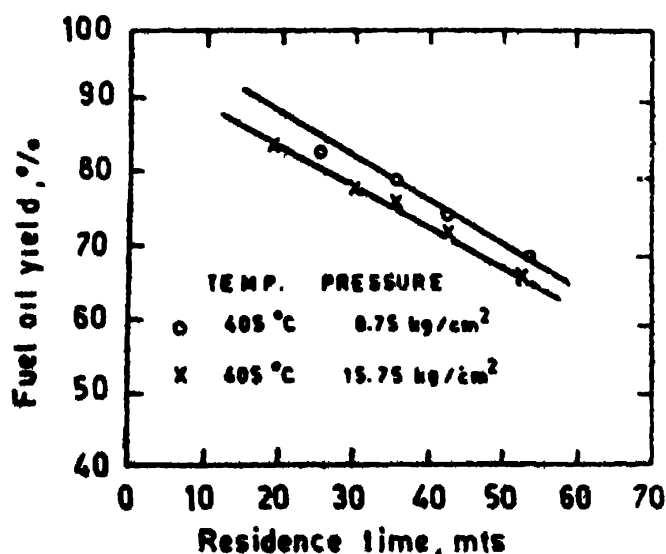


FIG. 5.2(a) Yield of Fuel oil as a function of Residence time and Pressure

ing time and temperature, light fractions increase, which correspondingly decreases the fuel oil yield. Though pressure has no

profound effect on liquid products, still a decrease in gas quantity at increased pressure is a usual happening.

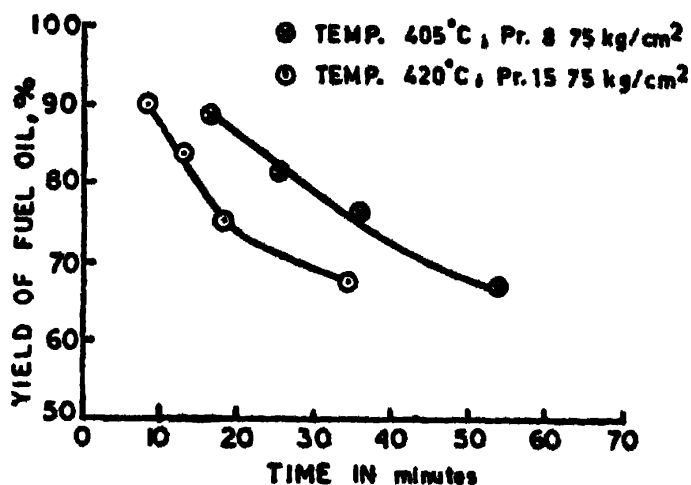


FIG. 5.2(b) Yield of Fuel oil as a function of time

5.1.3 CRACKING FOR PRODUCTION OF GASOLINE

Each stock has certain characteristics that govern the operating conditions during cracking. These set conditions shall satisfactorily yield the selected product to desired level. But the mixed stocks (or recycle oils) crack at more stringent temperatures. This can be separately met by devoting another coil exclusively for such refractory stocks. Modern refineries have anticipated such situations and instituted four coil furnaces. Each coil in such furnace can carry out specific duties. To elaborate further, one coil may be assigned to visbreaking operations (low temperature and pressure). Second coil may be reserved for cracking heavy oils where temperature and pressure may be 520°C and 25-35 atmospheres respectively. Like this, the other two coils may be operating at different conditions (for reforming or treatment techniques etc.). This type of furnace excels the other heating methods in rendering economic benefits to the refiner. Present pipe still heaters are capable of raising the temperature of feed stock to 500°C in a short time, may be less than three minutes.

Cracked products leaving at that high temperature are still active with abundant free radicals, hence immediate quenching is indispensable. For economic reasons quenching is deliberately done with the fresh feed stock. This serves in addition to

extraction of heat from the products thus ceasing the free radical activity, as a partial stripper to remove any volatiles present in feed stock.

Production of gasoline from high boiling fractions, was in fact an old process, specially by thermal cracking operations. At present the old methods are not given any weightage, however, Dubbs two coil cracking process with its own reputations had continued to occupy a valuable position in thermal cracking operations till today.

5.1.3.1 *Dubbs Two coil cracking process*

To meet the mounting demands of gasoline, cracked gasoline was first produced by Burton in 1912. Ever since that time various processes are in service to meet the fast rising demands for gasoline. Presently, refiners are not fond of producing thermal gasoline due to the extolling performance of catalytic crackers. Growing tendency of using this Dubbs two-coil-cracking for production of fuel oils from residuums or cracker feed stocks is due to its capacity to handle less valuable feed stocks. Further considerable reduction in coke formation is a welcome advantage over other thermal cracking operations.

Fig. 5.3 furnishes the flow sheet of this process. Firstly, the reduced crude (F/S) enters the distillation column (4). Here

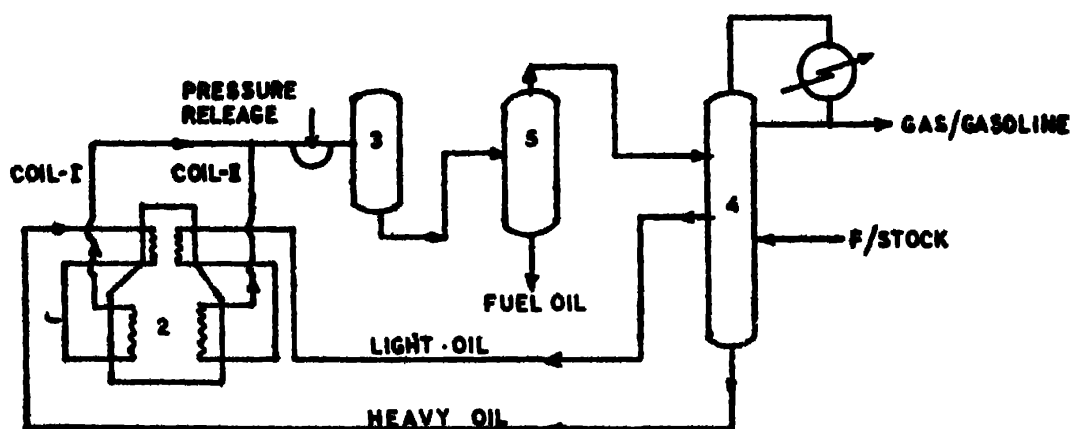


FIG. 5.3 Two coil cracking

extraction of heat from cracked products takes place; also any volatiles present in the feed are stripped off. From the bottom of the column heavy fraction is taken and cracked in a coil (1).

The temperature and pressure in this coil are maintained at 520°C and 30 atmospheres respectively. Light oil (circulating oil) a fraction obtained as a lower side cut from fractionation column (4), is routed through light oil coil (II), where the temperature shall be atleast 30°C higher than the other coil. The cracked products from both the coils are streamed into reaction chamber (3). Pressure in this chamber is maintained at 15 to 20 atmospheres. This pressure is essential to prevent excessive coke formation and increase liquid fractions. The products are now led into an evaporator (5) where heavy fraction is obtained from the bottom of the evaporator. Overhead fraction goes into fractionator (4). Heavy fraction from the evaporator is fuel oil and its pour point can be regulated to certain extent by recycle ratios of light to heavy oil. Usually, this ratio should be within 1 to 2. High severity and low recycling ratios result in better volatility and octane number of gasoline, although the quantity produced is less. With increasing severity, more gas and carbon formation are obvious. Gasoline, from low pressure operations is enriched with unsaturates and aromatics. An octane number of 70 is common, though it can be more if feed is more naphthenic. As a rule, sulfur in cracked products increase, though maximum concentration shall be in the bottom product. Gases are reported to be 50% unsaturated and form good feed stocks for polymer and alkylation purposes.

5.1.3.2 *Suspensoid Catalytic Cracking*

This is once through process, and owes its birth from thermal cracking operations. Main idea of this process is to deposit all the coke that is formed in the operation on catalyst itself.

The process consists of first mixing the catalyst and feed stock in proportion and passing through heater. Cracking takes place in presence of catalyst. At the delivery end the products of cracking are separated from the catalyst in a separator. Heavy fraction (tar) with catalyst particles is carried to a filter, where separation of catalyst takes place. Carbon on the catalyst is burnt off. In this operation high temperatures can be used.

5.2 **Catalytic Cracking**

Catalytic cracking is the most widely used refinery process

for converting heavy oils into gasoline of high octane value. This forms the heart of U.S. Refineries and is reputed to remove the ill effects of thermal cracking, such as unsaturation of products, high carbon formations and low yields of gasoline. In 1955 catalytic cracking capacity of the World was 13.3% of crude, while this is reported to be 6.9% in 1966, though in this decade demand for gasoline remarkably doubled. Alternative methods of production of quality gasoline have successfully permeated into industry.

Basically, catalytic cracking is distinguished from thermal cracking in the reaction mechanism, which is called carbonium ion mechanism. Carbonium ion mechanism reckons with the formation of more stable saturated compounds with abundance of isomeric reactions accompanying. The stability of these ions is mainly guided by the nature of molecule undergoing cracking, than the environments of cracking.

5.2.1 CARBONIUM ION CHEMISTRY

Most of the reactions like alkylation, polymerisation, cat. cracking, hydrocracking, reforming etc., involve organic chemistry of carbonium⁷ ion. Unlike free radicals, these are charged groups. A positively charged organic ion acting in chemical reactions, as if the charge were localised on one carbon atom, is known as carbonium ion. Electrophillic additions (Lewis acids) give such kind of charged ions. The formation of such ions is known as protonation (with Bronsted acids).

Protonation of an olefin

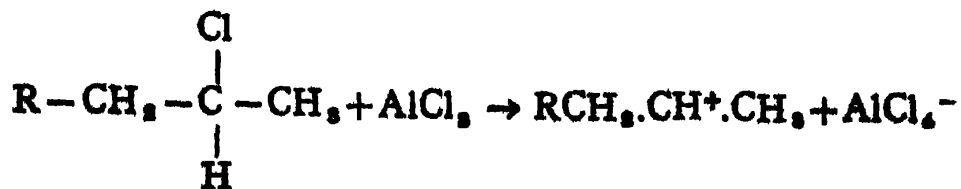


Additions of Lewis acids

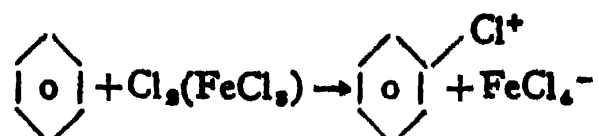


and the $(BF_3 + F)$ reaction goes on till $(RCHFCH_2F)_n B$ results.

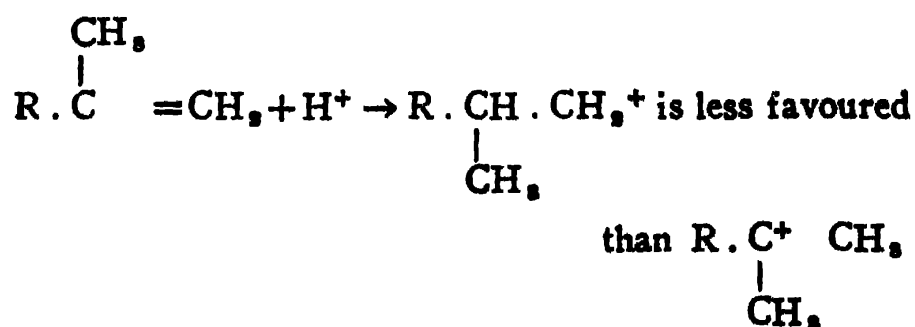
Breaking of carbon halogen bond



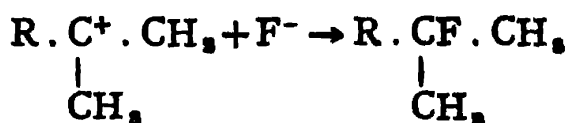
Aromatics react with electrophiles (Cl^+)



The life time of a carbonium ion may vary from a fraction of second to minutes (indyl cations exist even for months in sulfuric acid). Tertiary carbonium ion is the stablest one followed by secondary and primary carbonium ions. When protonation takes place, a primary carbonium ion may result,

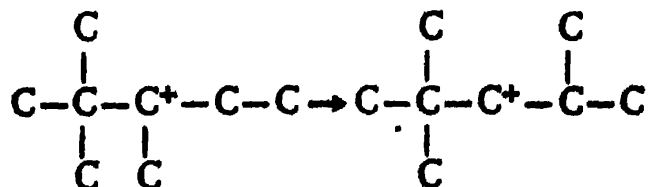


Now addition takes place according to Markovnikov's rule

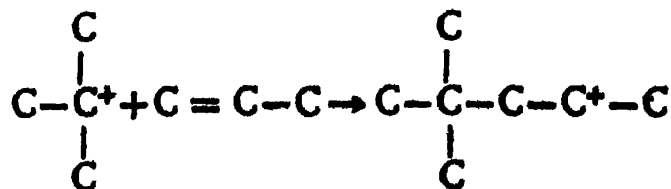


Number of steps are involved in these reactions like (a) proton elimination, (b) hydride shift, (c) methyl shift, (d) addition, (e) cracking, (f) hydride transfer, (g) termination of carbonium ions.

Methyl shift is similar to hydride shift

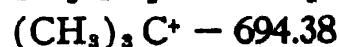
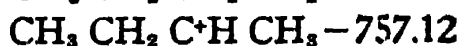
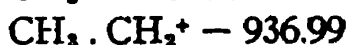
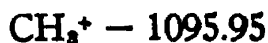


Addition to an olefin



undergo hydrogen transfer to produce aromatics, is a good example of such transfer.

Heats of formation of unsolvated carbonium ions. kJ/mole.



The heats of formation show that methyl, ethyl, ions have very high values, this explains why catalytic cracking yields little methane, ethane or ethylene.

Reviews of Sittig⁹ provide an excellent thesis on the subject of early 50's. Earlier catalysts of importance were silica-alumina type; the introduction of zeolite catalysts containing Ca, Mn or rare earths have really boosted the industry with unexpected dividends. All these catalysts subscribe to acid sites (Bronsted) that cause protonation.

5.2.1 Feed stock and Catalytic cracking conditions

Catalytic cracking is conducted relatively at less severe conditions. Temperature in all catalytic cracking operations lies in the range of 450-510°C; pressure, although specified for each type of reactor, does not exceed two atmospheres in fluidized bed reactors. In addition to these operating variables, catalyst to oil ratio is a set factor for a particular kind of operation.

Feed of catalytic crackers is gas oils or blends of thermally cracked oils. With modern tendency to utilise even residuums or solvent extracts, the feed characteristics are more decisive. Feed stocks generally contain sulfur and nitrogen; these with metals present in oil, give trouble to the refiners. Sulfur and oxygen compounds exhibit pugnacious effects on catalysts. Nitrogen though available in small quantity; 30 to 50% of it is frequently basic. This harms the catalyst by reacting with acid sites. Voltz et⁹ al discussed the effect of basic nitrogen on conversion rates and on decay coefficient of catalyst (see Table 5.4).

TABLE 5.4 EFFECT OF NITROGEN ON CRACKING

	Crack- ing Temp.	K_0	K_1	K_2	Decay-co- efficient
Midcontinent gas oil (a)	536	42.7	33.1	3.59	32.8
Fresh oil (b)	494	28.4	24.1	2.07	33.4
+0.1% wt. of basic nitrogen					
(a) + 0.1% „ 536		22.5	17.2	2.21	30.5
(b) + -do- „ 494		13.8	10.3	0.22	29.3
(a) +0.2% wt. of basic nitrogen					
536		16.3	12.7	1.97	27.3

where, K_0 = rate const. for gas oil cracking, K_1 = rate const. for gasoline formation, K_2 = rate const. for gasoline cracking.

At least half of the known metals are present in petroleum, although in traces¹⁰, such as vanadium, nickel, iron, copper, etc. restrain the functions of catalyst by effectively blinding the active sites. Straight run and vacuum gas oils are relatively free from such metallic bodies, but residuums definitely call for special attention. The ability to feed the heavier portion of crudes to Fluid Catalytic Cracker, depends to some extent on vanadium and nickel content. Phillips Research and Development¹¹ Facilities devised a process using an additive containing antimony that will passivate the metal contaminants. By this way catalysts may be able to take up feeds of 12,000 ppm of nickel vanadium complexes. Conradson carbon residue of the stocks should be kept well below 4% to limit carbon formation.

Pretreatment of such stocks is immensely regarded as beneficial to catalytic cracking operations, not only in safeguarding the life of catalyst, but also saving the time and amount in purifying each fraction. Sulfuric acid treatment furnishes effective removal of sulfur and nitrogen compounds. 85% acid

strength is common for such treatments. Even some of the base metals may be dissolved, but the probability of elimination of the metals by sulfuric acid is not satisfactory. Phenol or furfural treatment is indispensable for aromatic (condensates) rich stocks. Deasphalting of residuums generally eliminate—highly condensed structures. These condensed structures contain metals too, in addition to sulfur and nitrogen bearing resins. Sulfur present in aromatics usually favours more coke formation during cracking.

5.2.2 CATALYTIC CRACKERS—TYPES—WORKING

Catalytic cracking is conducted over fixed beds or in moving beds. 20% of catalytic cracking¹² as it stands now is done by moving beds; while 80% of cracking is left with fluidized beds, fixed beds are now obsolete. Pellet form catalysts are suitable for fixed bed operations, while moving beds function with beads. Moving beds, initially, used bucket elevators to lift the catalyst upto disengager but now air lifts have successfully replaced such mechanical designs. Zeolite catalysts¹³ in the form of beads (of Calcium, Manganese and rare earths) are new arrivals in this field since 1965, and the commercial production of these has become immense. Dura bead type catalyst preparations¹⁴ or even zeolite catalysts with active sites crack ten times more than low alumina catalysts or twice as much as high alumina catalysts. Cracking with less deposition of coke on surface of catalyst is an admirable thing with these zeolites. At 70% conversion, zeolites yielded only 6% coke while low alumina catalysts produced twice this amount. Yield of gasoline is also up by 10% with zeolites. (See Table 5.5). Zeolites further improve the selectivity characteristics that may result in quality rather than in quantity of products. Gulf's FCC¹⁵ catalysts were developed to suit high temperature operations, that usually happens in short contact risers. These produce 7% more yields of gasoline than the long contact risers. Short contact risers are capable of producing gases rich in olefins. Moving and fluidized beds sustain the endothermic cracking reactions with the residual heat left in the catalyst during regeneration. Regenerators and reactors are placed close enough to save the heat energy of the operation. Perfect heat balance in reactor and regenerator system is left

with adulation. However, fixed beds have to survive by constant circulation of molten salt from regenerator to reactor, the only method of supplying heat. Obvious advantages of fluidized and moving beds have terminated the expansion of fixed beds. The old units are still continuing, without any advancement.

Recycling is a common phenomena with some types of feed. and fresh feed to recycle stocks¹⁸ are kept in 1 : 2 to 5 : 1.

TABLE 5.5

FLUID BED CRACKER YIELDS WITH DIFFERENT CATALYSTS

	Low alumina	High alumina	Zeolites
Conversion %	61	68	74
C ₁ +C ₂ +H ₂ wt %	1.674	1.672	1.755
C ₃ % vol.	8.4	8.2	7.4
C ₄ % vol.	6.2	7.4	9.4
Gasoline % vol.	50.5	58.0	63.5
LGO % vol.	12	14	13
Coke % wt.	6.0	6.0	6.0

5.2.2.1 *Reaction Variables*

Pressure, temperature and catalyst to oil ratio are the usual parameters that take care of cracking. Catalyst to oil ratio is a variable factor, as the activity of catalyst swiftly diminishes with usage. Even after regeneration the carbon content of catalyst does not go below 0.25% ; this causes fatigue in catalysts, consequent effect of which is improper cracking. Surface area is another factor ; the sharp drop in such active area in equilibrium catalysts, followed by increase in bulk density with cracking time, vastly reduces the conversions. Thus, catalyst oil ratio, catalyst activity and space velocity should be treated as dependent variables in the reactor operation. Physical composition and some important properties of catalysts used in moving beds and FCC units are shown in Tables 5.6 and 7. .

Reactor temperature and pressure are truly independent variables. In short contact risers (where the time of contact between oil and catalyst lies between 1 to 4 sec)¹⁷, a high improvement in octane¹⁸ quality is achieved due to cracking at higher temperatures. Pressure has no direct impact on cracking reactions. Pressure is often set by the unit capacity. Regenerator pressure is always coupled to the reactor system. The increase in partial pressure of oil causes much coke formation. Catalyst being a fine powder in FCC units excessive regeneration pressure will give problems.

TABLE 56 MOVING BED CATALYSTS^{9'b}

Chemical composition	Durabead catalysts (two types No. 1 & 5)			
	No. 1		No. 5	
	Fresh	Equilibrium	Fresh	Equilibrium
SiO ₂	90		85	
Al ₂ O ₃	9.7		12	
Cr ₂ O ₃	0.15		0.15	
Na	0.1		0.1	
SO ₄	0.1		0.1	
Rare earth oxide	—		2.5	
Density gm/cc	0.7	0.78	0.67	0.73
Particle dia mm	3.5 to 3.6	3.1	3.5 to 3.6	3.1
Surface area sq m/gm	195	85	200	135
Average pore dia °A	72	141	92	110

TABLE 5.7 : COMPARISON OF PROPERTIES^(a) OF FRESH AND EQUILIBRIUM FCC CATALYSTS

	Amorphous high alumina		Zeolite XZ-2	
	Fresh	Equilibrium	Fresh	Equilibrium
Chemical analysis (dry basis), wt.%				
Alumina ^b	28	21.5	31	25.4
Carbon	0	0.20	0	0.25
Sulfate	0.7	0.1	0.3	0.1
Sodium	0.03	0.02	0.04	0.04
Iron (ppm)	300	3900	700	3700
Metals (ppm of V+Ni+Cu)	0	162	0	259
Physical properties				
Surface area, m ² /g	415	140	335	97
Pore Volume, cm ³ /g	0.88	0.43	0.60	0.45
Av. bulk density g/cm ³	0.39	0.70	0.52	0.68
Particle size, micronesh sieves, wt %				
0 to 20 μ m	2	0	2	0
0 to 40 μ m	17	8	19	6
0 to 80 μ m	68	69	75	75
Av. particle size, μ m	65	63	62	62
Catalytic activity Microactivity, vol.%				
Conversion	60 ^c	59 ^c	85	73
Carbon factor	1.0	1.1	0.6	0.6
Hydrogen factor	1.0	1.1	0.2	0.7

(a) By courtesy (Marcel Dekker inc, New York) taken from "FLUID CATALYTIC CRACKING with Zeolites" by Paul B Venuto, p 46.

(b) Equilibrium values are low due to presence of some residual low alumina of long age.

(c) After 24 hr/1050°F/60 psig, 100% steam.

5.2.2.2 *Impact of catalyst to oil contact time on selectivity*

60% of total conversion results in short contact risers where time of contact between oil and catalyst may not exceed 4 seconds. Catalyst separation is done immediately after effluents leave the riser. This is achieved to a maximum extent by decreasing the velocity. The dense bed environments cause back mixing and lead to secondary reactions which contribute excessive coke formations. Avoiding such contacts may be possible by direct admission of vapours into cyclones. In the riser system¹⁰ the activity and selectivity of the catalyst is largely maintained till the cracking is over ; and coke does not build up so rapidly in this period.

5.2.3 CATALYTIC CRACKING PROCESSES

- (1) Fixed bed, Houdry.
- (2) Moving beds—Air lift- -Thermofor catalytic cracking Houdri-flow.
- (3) Fluidised Beds : (a) Gulf Research (Fluid catalytic cracking) FCC, UOP, Texaco.
(b) Kellog (Ortho flow)
(c) ESSO—Flexi cracking
(d) Standard oil—Ultra cracking.

5.2.3.1 *Fixed Bed Crackers*

Fig. 5.4 illustrates Houdry Fixed bed process. At present, though no new plants based on this technology are being set up the old ones still continuing. There are three reactors in parallel (1,2 & 3), in this system. At the bottom of each reactor there are four connections (V_1 , V_2 , V_3 , and V_4) provided through a rotary disc. Only one line at a time is to be connected to the reactor ; when the first reactor is on process stream, 2nd reactor will be on steam purge followed by air purge, and the 3rd reactor will be in regeneration process. At the start, charge oil vapor, free from tar, will enter the reactor through valve V_1 . After cracking, the vapours escape through the reactor outlet as product and go to the fractionator through line a_1 . (At the top of the reactor also ; same type of rotary arrangement is there, but connects only three valves ; these valves connect line a_1 for products ; a_2 for air outlet and a_3 for steam purge alternatively.)

Immediately the reactor is disconnected and connected with steam line (from top) through line a_3 and exhausted through the bottom (V_4). Oil vapours from this exhaust are condensed

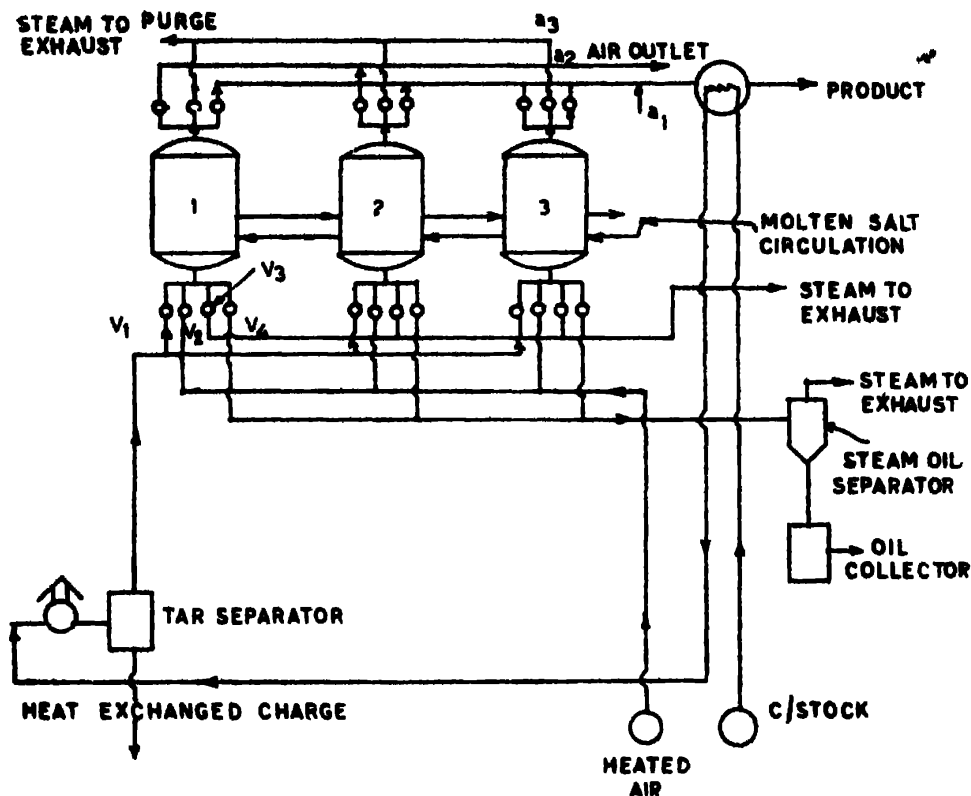


FIG. 54. Houdry fixed bed process

and steam is allowed to leave the separator. During this purging operation, 2nd reactor will be on steam. Soon purging operation is over, preheated air is sent into reactor 1, through valve V_2 and flue gas goes off through line a_2 at the top of the reactor. After regeneration steam purging from top to bottom is again conducted and exhaust steam is taken out through valve V_3 from the bottom of reactor. When downward steam purging takes place, 2nd reactor has to be disconnected and 3rd reactor will be connected to main stream. Rotary valves with interlocking system conducts smooth automatic cycling of the reactors. Molten salt is circulated to reactor, from the reactor under regeneration, to supply necessary heat. Molten salt maintains the heat of reaction in each reactor through extracting heat from the regenerator and supplying it. The valves are rotary type and

interlocked so that manual error cannot result. Usual cyclic operation consists of the following :

1. On stream 10 minutes.
2. Downward purging of steam to recover hydrocarbons—5 min.
3. Regenerations by blowing hot air through bottom of the reactor—10 min.
4. Air purge followed by steam purge downward—5 min.

It can be seen that *on stream* will be equal to regeneration period ; which will be equal to the sum of steam purging periods, before and after regeneration.

Operating conditions

Reactor temperature—450 to 520°C

Operating pressure (gauge)—1 to 2 kg/cm²

Space velocity (Liquid)—1 to 1.75 (1/Hr.)

Regeneration temperature—upto 520°C

Air pressure, during regeneration—upto 4 kg/cm²

Catalyst shape—Beads/pellets

Composition—Silica-alumina

Catalyst processing capacity—20 to 40 Bbls/kg.

Vapor inlet temperature—430°C.

5.2.3.2 *Moving Bed Crackers*

Thermoform catalytic cracking units fall into this category. Catalyst shape in these units may be spherical or beads. The shape and size of the catalyst permit free flow of catalyst in the reactor. Catalyst and oil move cocurrently from top to bottom in the reactor. Reactor is stacked directly over the regenerator as shown in Fig. 5.5. In between reactor and regenerator there is a constriction, where steam purging is done. This helps firstly in removing hydrocarbons from the surface of catalyst, secondly steam prevents the reactor products from going downwards into regenerator ; which is highly essential otherwise the situation may become unwarranted.

Spent catalyst is regenerated by air blowing. The flue gas passes through cyclone separators, leaving catalyst dust, if any, in the out going stream. At the bottom of regenerator, there is a

cooling section to cool the catalyst. Such regenerators shall be in two numbers, kept below the reactor. The catalyst collected from the regenerator is lifted into catalyst disengager, placed

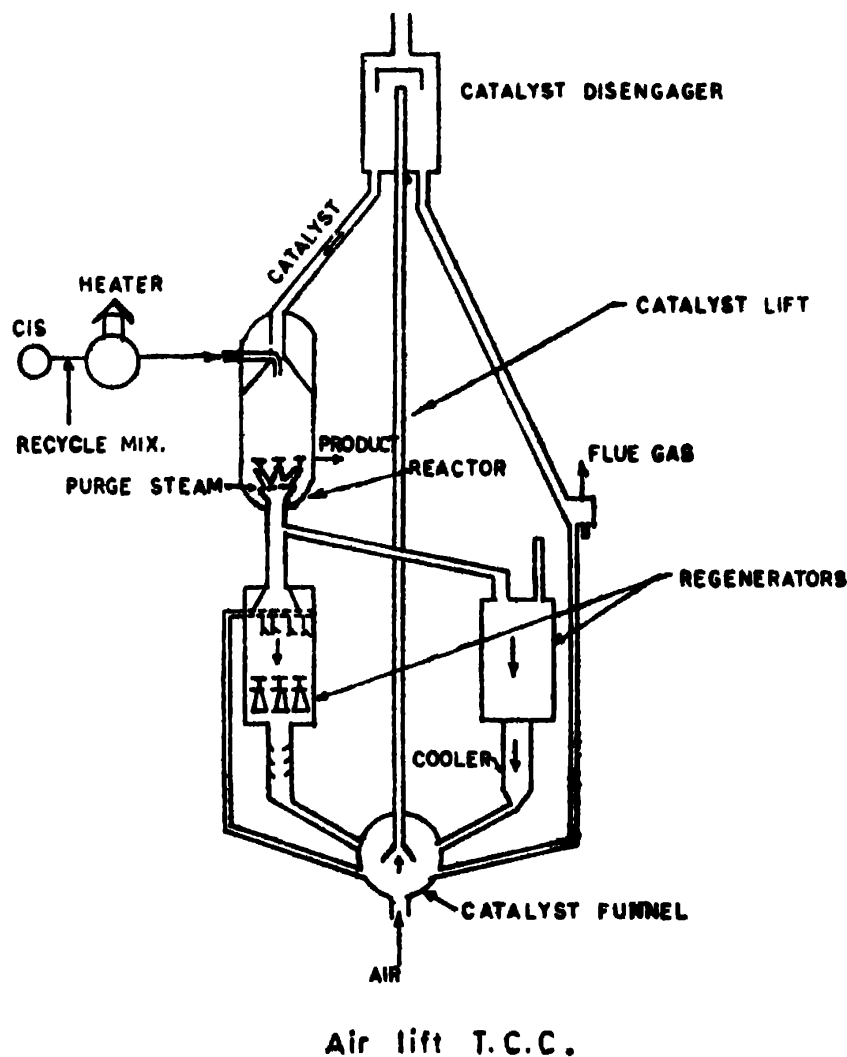


FIG. 55. Air lift thermoform catalytic cracker

at a height more than the reactor, which automatically feed the catalyst into reactor due to gravity. Old designs employed bucket elevators to lift the catalyst, while modern practice is to use air. Thus the name Air lift Thermoform catalytic cracking has been accomplished. Catalyst from both the regenerators is conveyed into a single funnel, from where the pneumatic conveyance can take place. Feed and catalyst always travel downwardly in the reactor, and products escape from the side of reactor. Proper distribution of catalyst for good performance

is essential. The disadvantage of this process is in low catalyst to oil ratio which increases the coke deposition on catalyst.

Operating conditions

Regeneration Temperature	600°C
Recycle ratio	0-0.5 Vol./vol.
Catalyst to oil ratio	2 to 7
Space velocity	0.7 V/hr. V.
Catalyst shape	beads
Vapour inlet Temp. °C	500
Catalyst Temp. °C	515
Reactor pressure	3 kg/cm ²

5.2.3.3 Houdri Flow Process

Houdri flow process is distinguished from the TCC process in its (a) ease of operation (b) low cost of maintenance (c) high catalytic activity (low catalyst make up costs) (d) flexibility in handling charge stocks and conversions attained.

In this design, reactor is placed above the regenerator, in

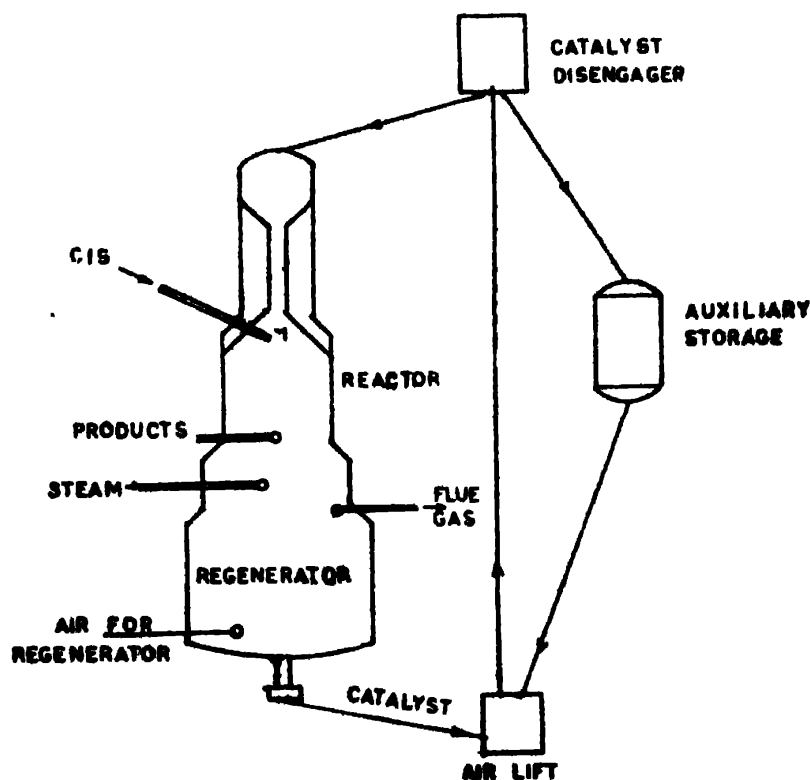


FIG. 5.6. Houdri flow catalytic cracking

a single shell. The regenerated catalyst (either natural or synthetic type) is carried by pneumatic lift to disengager, from where the catalyst can either go into reactor or auxiliary storage bin. The system works on self heat balance, so no additional heating or cooling of catalyst is anticipated. Usually operations^{20-a} are conducted in temperature range of 450-520°C, at pressure 1.5 to 2 atmos; with a space velocity of 1.5 to 4 V/hr./V_c. Catalyst to oil ratio of 3 to 7 is maintained with high recycle ratios of 1 : 1. A conversion of 90% can be obtained with recycling, while once through cracking permits a conversion of 60%. The octane value of gasoline lies in the range of 85 to 90. Yield can be improved by using zeolite catalysts. Fiv. 5.6 shows the flow diagram of the above process

Houdri flow yields²¹

Naphthenic gas oil	BPSD	API		
Charge	4200	32.6		
Recycle	4200	31.7		
Total	8400	32.0		
Products			Vol %	Wt%
C ₂ & Lighter	—	—	—	3.9
C ₃	306	—	7.3	4.4
C ₄	714	—	17.0	11.5
Gasoline (FBP 215°C)	2705	59.7	64.4	55.2
LGO	521	31.0	12.4	12.5
HGO	200	—	4.8	4.9
Coke	—	—	—	7.6

5.2.4 FLUID CATALYTIC CRACKING (FCC Complex and Hardware)

Fluid catalytic cracking enjoys an impregnable position in catalytic cracking operations. All types of fractions from naphtha to deasphalated oils can conveniently form the feed stocks. Numerous designs of FCC units have appeared in the literature^{22a}. The FCC complex usually consists of three major sections :

- (a) Reactor-riser
- (b) Regenerator-flue gas separation
- (c) Distillation and recycling.

Associated with the cracker, other units like polymerisation, alkylation are maintained for gaining economy.

Reactor riser design had been subjected to number of changes since its inception and still better types of risers are being introduced. The function of the riser is in fact to bring a thorough contact between vapor and catalyst in a short time^{22b}; short contact times are less than 5 seconds. In the reactor, the cracked oil vapours escape through a perfect separation system, that is an inbuilt cyclone system. Disengaged catalyst, from cyclones falls into reactor and is steam stripped. The catalyst is then regenerated after burning off the coke in a separate unit, i.e. regenerator. Fluidisation is carried out in dense phase and dilute phase. Dense phase is prevalent in the bottom portion of the reactor, while dilute bed prevails in the upper part of reactor.

Cracking in risers

From the moment of contact between oil and catalyst at the point of introduction in the riser, the complexity of reactions go on increasing as the material move through the riser.

With increasing cracking, deposition of coke, degradation in catalyst²³ activity and a sharp increase in velocity of vapour

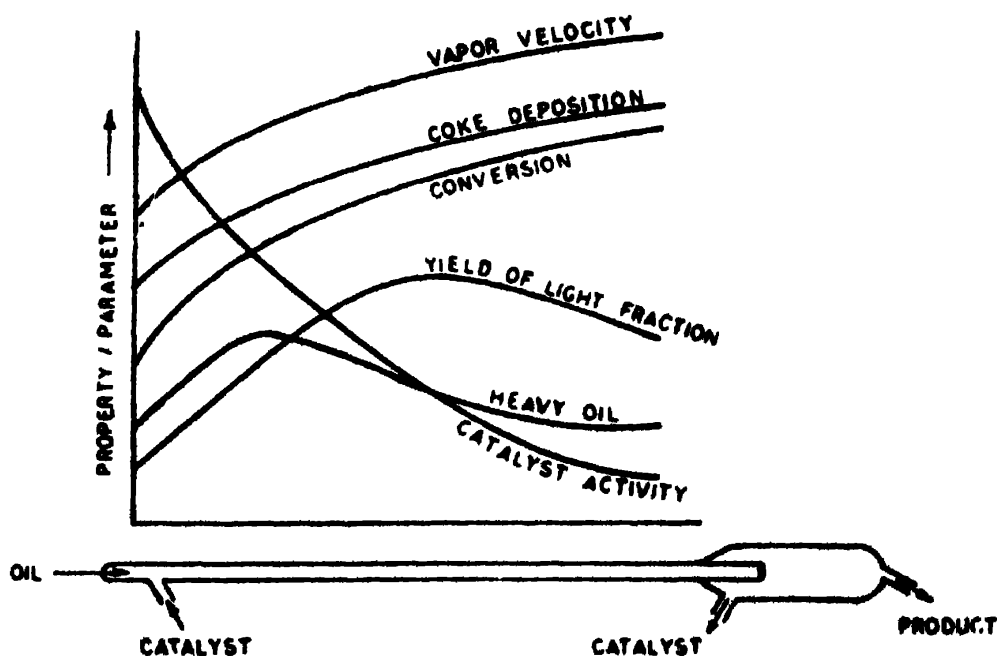


FIG. 5.7. Profiles of different Parameters in a riser cracker with distance

are some inherent complications. Though the increase in velocity of vapour is regarded as a benefit to fluidization, the relative velocity (slip velocity) between catalyst and oil decreases, and the result is improper cracking. In the Figure 5.7 the profiles of various parameters with respect to height of riser is shown.

Slip velocity is defined as the velocity of vapor divided by velocity of catalyst²⁴.

$$\text{Slip velocity : } \frac{V_v}{V_c}$$

where,

V_v velocity of vapor

V_c velocity of catalyst

The terminal velocity of catalyst particle may become the difference in these two velocities hence the slip velocity can be rewritten as

$$\text{Slip velocity} = \frac{V_v}{V_v - V_t}$$

where,

V_t is terminal velocity of particle,

V_v velocity of vapor

Generally the slip velocity should be of the order 1.5. Each configuration has its own riser design, assembly of reactor, regenerator and fractionator.

An ideal addition and recovery system for fluid catalytic cracker would be one, which minimises additions of fresh catalyst and maintains an optimum size distribution of circulating equilibrium catalyst. In fact, loss, frequency of withdrawal of catalyst (equilibrium) are all functions of quality and quantity of fresh catalyst added. Factors affecting the FCC operations²⁵ are usually, shrinkage, attrition, entrainment in cyclone systems and regeneration systems.

Fig. 5.8 shows the outlines of FCC unit designed by Texaco Development Corporation. In this design separate riser crackers are detailed for cracking fresh feed and recycled feed. In the reactor the variation in dense phase and dilute phase conditions

are supposed to be added advantages. Efficient reactor and the cyclone separator system furnish the necessary implements to process feed stocks of different types.

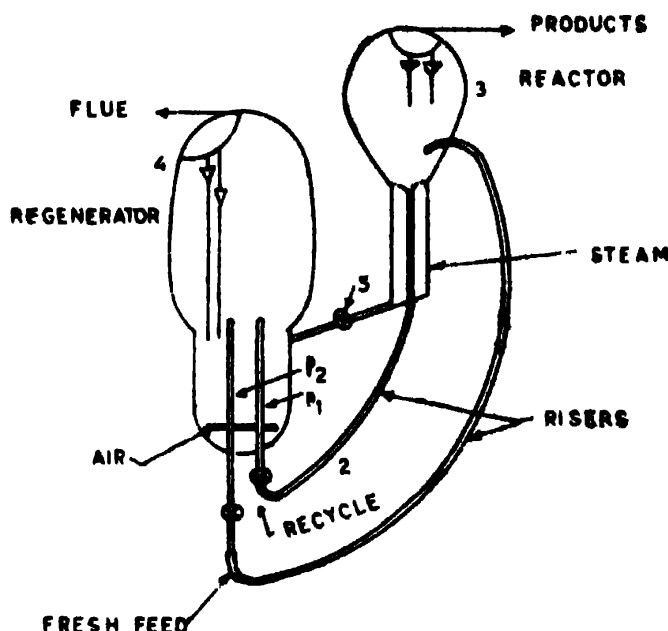


FIG 58 Fluid catalytic cracking

Preheated stock is mixed with catalyst at the bottom bend of the fresh feed riser (1). The products and catalyst enter the reactor space (3) in dilute phase, the catalyst disengages from vapours. The vapours are freed from catalyst dust in cyclone system. Recycle stock is permitted to enter through the other riser (2). It mixes here with regenerated catalyst and goes into reactor space. The fresh feed riser directs the products downwardly in the reactor, while recycled stock riser delivers vertically into the reactor space. Vapours from both the risers join together and go for fractionation through cyclones. Cyclones are situated in the reactor and regenerator, so that the catalyst dust can be caught.

The spent catalyst from the reactor after steam stripping passes into regenerator (4) through a pipe (5). A blast of air burns off the coke on the catalyst particles and flue gas formed escapes through the cyclones into atmosphere. Regenerator in this design is provided with two channel pipes (p_1 & p_2). These

pipes are joined to risers. Through one riser, while fresh feed enters through the other one, recycled stocks enter, as mentioned already.

5.2.4.1 Flexi Cracking

Flexi cracking, developed by ESSO, offers two reactor configurations: and gives operating flexibility and expansion capacity.

Fig. 5.9(a) shows riser cracker model. In normal operations, the riser cracker operates with no dense phase bed in the

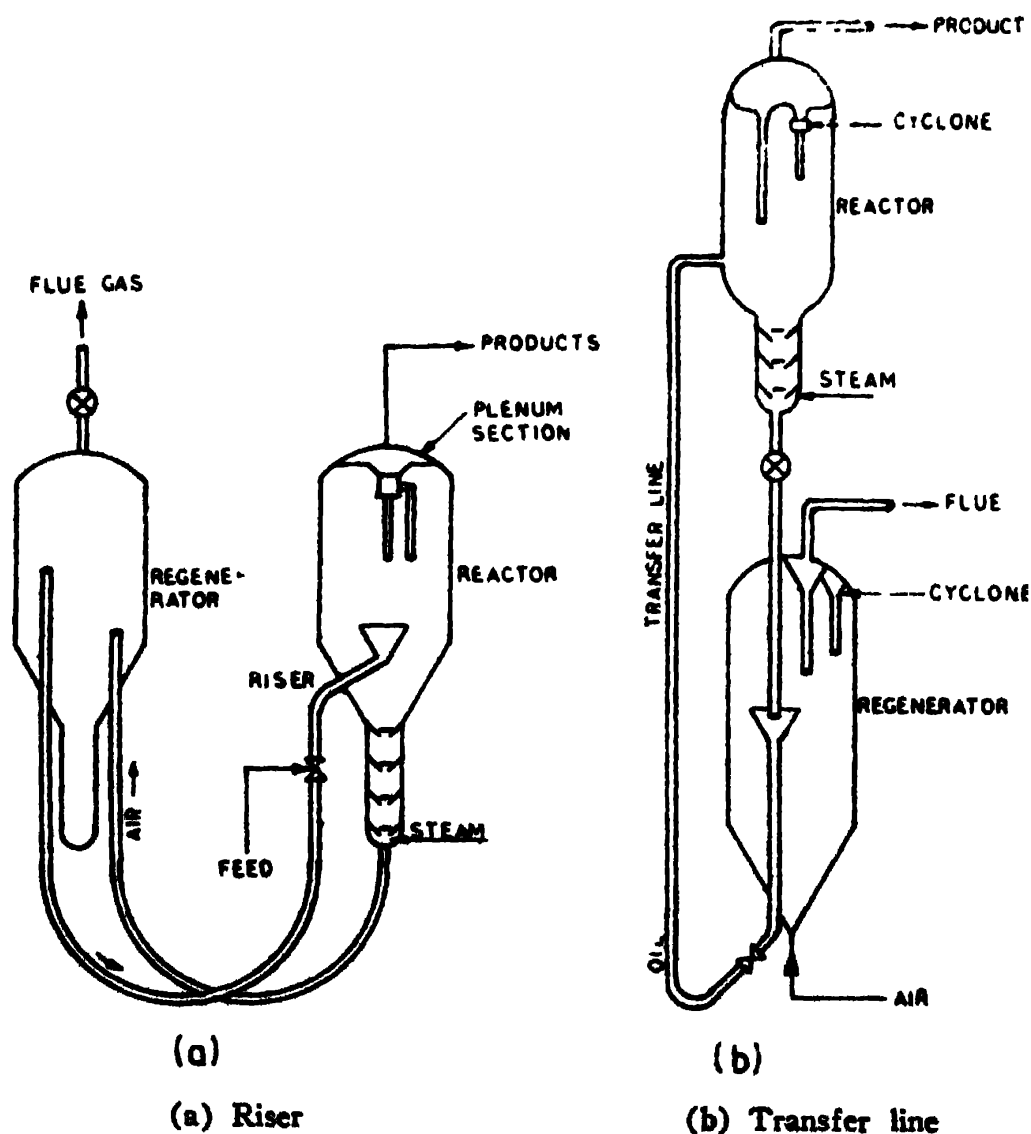


FIG. 5.9. Flexi cracking Models

reactor. In this model high space velocities of 50^{ss} (weight/hr/weight) are maintained to enhance the advantages of zeolite catalysts. Maximum liquid products and least problems in handling different feed stocks are considered to be the major benefits of this assembly. The riser cracker can work on variable space velocities ranging from 50 to 5 (V/hr/V). The cyclones in the reactor are designed to provide plug flow of catalyst without back mixing the oil with catalyst. The latest modification of U bend design differs from the previous one, which abruptly changes the direction of catalyst and flow lines. Side by side reactor and regenerator placement furnishes smooth control in catalyst circulation. Model IV removes the disadvantages of the previous ones by increased recovery in catalysts and free switching of naphtha to reduced crudes. The overall yield of gasoline may be of the order of 70% with low gas yields. The percentage of olefin content in the gases can be increased to as high as 55% by proper adjustment of the variables.

The second configuration Fig. 5.9(b) is pure transfer line configuration. In this design all the cracking takes place in transfer line, and the reaction is rapidly terminated by disengaging oil from catalyst in a cyclone separator. High to low space velocities can be worked out in this model depending upon the quality of feed. These two configurations can cover adequately the needs of a refinery either for expansion or switching to process different feed stocks. These two configurations cover about 2,000,000 bpsd or 25% of the free world capacity.

Silica-manganese type catalyst or natural catalysts with activated earths are also tried in the above configurations for better conversions.

5.2.4.2 *Ortho Flow Reactor*

Ortho flow riser reactor developed by Kellogg is highly selective in converting heavy petroleum fractions to valuable light olefins and furnace oils in addition to gasoline.

Fig. 5.10 shows the ortho flow reactor. It covers the specific needs of the refiner in converting low value feed stocks to high value products, with less investment and operating costs. Variety yields can be obtained by sacrificing efficiency. The cracking takes place in the riser²⁷ part of the reactor.

The fresh feed enters into external riser at the point where it becomes vertical, as shown in figure. Catalyst fluidised by

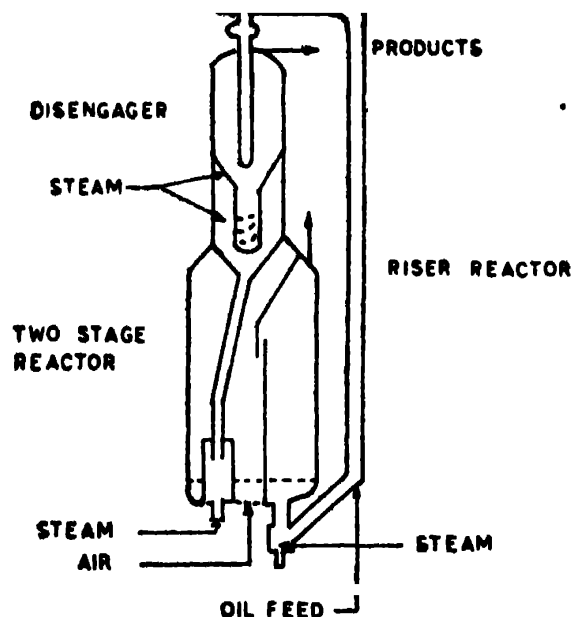


FIG 5 10. Orthoflow reactor

steam from the stripper enters the riser. Oil and catalyst mix in this riser, where craking takes place. Cracked products now enter the disengager, where the catalyst is separated. The products escape through a cyclone. The catalyst is stripped off with steam. Hydrocarbon free catalyst then enters the regenerator, where it is regenerated by blowing air either in one or two stages. After regeneration the catalyst is steam stripped and fluidised to enter the riser crackcr to repeat the cycle. The riser part may be kept in the reactor-regeneration combination itself when it is called internal riser model.

Operating^{20-b} conditions

Temperature	—	470-500°C
Pressure	—	1.5 to 2.2 atm.
Regenerator temperature :		580-610°C
Pressure	—	1.3 kg/cm ²
Cat/feed	—	2.5 to 5 kgs/bbl.

In India¹ catalytic cracking practice is not very much. Approximately 3% of the crude refined is used for this purpose.

There are two units of FCC, situated one each in Bombay and Vizag Refineries (Hindustan Petroleum). One of these two is designed to crack heavy distillates of Iranian crude (350 to 550°C).

The following data belongs to the same unit

Cat. cracker operating pressure 1.43 Kg/cm²

Feed Temperature 315.5°C

Cat. hold up 15 tons in cracker
 19 tons in regenerators

Particle size 40-80 -70 to 80%
(Microns) 0 -40 — 5 to 7%

Surface area of the catalyst 500 to 600 m²/gm (fresh)
 200 m²/gm (used)

Cat. circulation 8 tons per hour

Capacity 7,500 BPSD

Reactor temperature 465- 510°C

Oil feed temperature 315- 455°C

Regenerator temp. 593- 675°C

Dense phase temp. 660°C

Plenum chamber temp 680°C

Spent riser temperature 470°C

Cat loss 1.4 tons/day

Coke yield 3.8 %

Steam rate at 9 Kg/cm² with 20° superheat.

Injection	370	Kg/hr.
Stripping	1260	
Process	150	

Yields

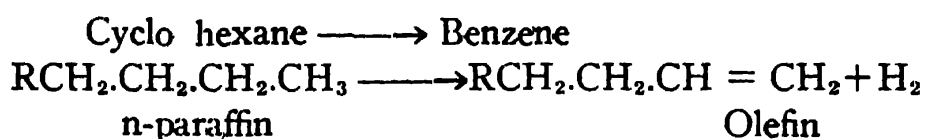
Gas	1.9%
L P G	13.0%
Gasoline	18.8
Kerosene	16.0
Light gas oil	11.6
Heavy gas oil	26.4
Tar	12.3

5.3 Catalytic Reforming

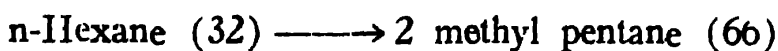
INTRODUCTION AND THEORY

With the advent of I.C. engines of high compression ratio, the quality of fuel had to undergo changes. Prevention of knocking under such compression ratios, is achieved by increase in the octane value of the fuel. Upgrading low octane gasolines catalytically is known as catalytic reforming. Thermal reforming can also be practised, but not desirable due to the inherent disadvantages. The octane rating improvement is accomplished chiefly by reorienting or re-forming the low octane components into high octane components. Much desired reformate is influenced by the characteristics of feed stock and catalyst. The reactions, reckoned of general occurrence are given below :

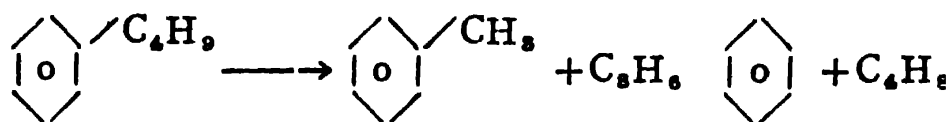
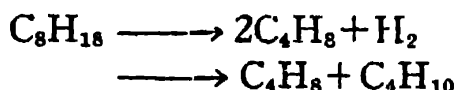
(a) Dehydrogenation (Saturates to unsaturates)



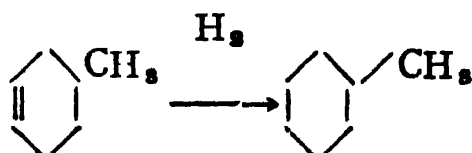
(b) isomerisation



(c) Paraffin cracking (chain cracking)

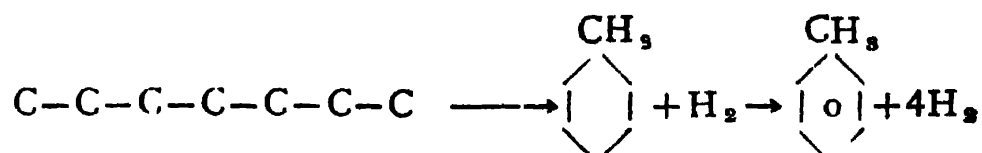


Hydrogenation of Unsaturates

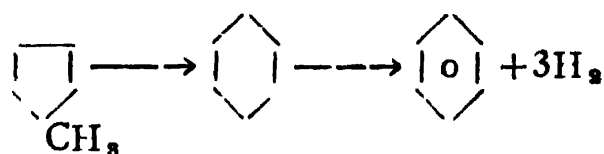


Methyl cyclohexene $\longrightarrow$ Methyl cyclohexane

Paraffin dehydro cyclisation



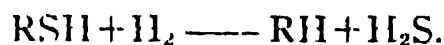
Naphthene isomerisation and dehydrogenation



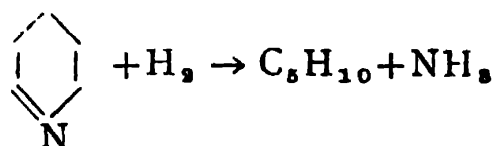
Methylpentane (91) (103)

(Figs in brackets show octane no.)

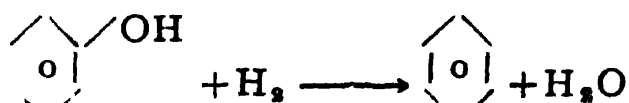
Hydrodesulfurisation



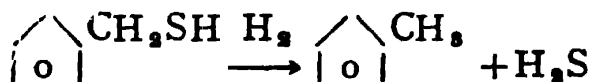
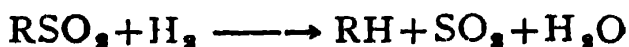
Denitrogenation



De oxidation



Combination reactions.



5.3.1 REACTIONS-CONDITIONS

All the above reactions are likely to occur to varying degrees. Isomerisation and dehydrogenation reactions are fast.²⁸ Cyclisation reactions are very slow and require severe conditions. Hydrocracking and other elimination reactions may be treated as slow reactions. However isomerisation and cyclisation reactions

are the best contributors of octane number. The proper and worthy reaction is dehydrogenation and cyclisation of n-paraffins; that results in a tangible improvement in octane rating (n-heptane of zero octane rating to more than 100 octane number).

Cracking reactions produce more lighter components which have better octane quality than the heavier ones; yet the reactions are not opted due to the fear of excessive coke formation on catalyst and unsaturation in the products. Vigorous hydrocracking is desirable when the feed stock is rich in paraffins.

5.3.1.1 *Effect of Pressure*

Low pressure encourages dehydrogenation reactions, while no noticeable effect of pressure on isomerisation may be expected. Coke formation is more at low pressures. Increase in pressure causes dealkylation very much. Hydrocracking and elimination reactions are directly related to the partial pressure of hydrogen.

5.3.1.2 *Effect of Temperature*

Except hydrogenation reactions, which are exothermic all other reactions are favoured by increasing temperature. With increase of temperature, chances of degradation of product, and coke deposition are likely. Hence for smooth operations, the amicable parameters instituted in a catalytic reformer must embrace all the above considerations.

For economic operations the parameters judiciously decided are

- (a) Low pressure (b) High temperature
- (c) High hydrogen circulation.

With increased coke deposition at low pressures, the reactors are preferably operated at 10 to 50 atmos pressure. Suitability of catalyst for such operations is to be decided beforehand. Improvement of octane quality is rapid with high catalyst to feed ratios, which restricts the operation to go for high space velocities. Indeed the space velocity does not exceed more than $3(V/hr/V)$

The temperature above 500°C promptly spoils the activity of catalyst. A temperature range of $450-500^{\circ}\text{C}$ is frequently

advisable and can bring about all reactions without much severe coking problems. All dehydrogenation reactions produce good amount of hydrogen; hydrogen is consumed to some extent in hydrogenation reactions, the remaining is available as by product. High circulation of hydrogen suppresses the coking tendency too.

In conclusion it may be stated that faster reactions will tend to predominate in short residence time operation, which results in maximum aromatics and hydrogen production. High temperatures give rise to high aromatic content. Naphthenic stocks with high hydrogen to hydrocarbon ratio are liable to affect adversely the yields.

5.3.2 CATALYSTS

In reforming many reactions are going together; hence a catalyst to maintain its activity towards all reactions equally is rare. Haensel²⁰ developed platinum catalysts and these are still being used with slight or no modifications. Acid sites, on catalyst are responsible for isomerisation and cyclisation reactions; while metallic bonds favour hydrogenation reactions. These two functions have to be met by a catalyst. For this reason, acid sites incorporation on platinum catalyst is unavoidable; eventually halogenation (upto 0.1%) has come into service. Platinum Catalysts are graded by the amount of platinum deposited on the base. Low platinum catalysts are non regenerative type. These contain 0.3% of platinum on silica or silica-alumina. High platinum catalysts contain 0.3 to 0.5% metal and form regenerative catalysts. The cost of platinum prohibits its trials in fluidised reactors. Moving bed units are however in operation, but their incessant use is doubtful.

Other catalysts suitable for such operations are chromium oxide and molybdenum oxide on alumina. These are very good catalysts for isomerisation and hydrogenation reactions. Chromium oxides and molybdenum oxides on silica or alumina or silica-alumina are quite abrasive resistant and can be used in moving beds and fluidised beds.

Approximate operating conditions with different catalysts is presented in Table 5.8(a).

High platinum Catalysts are frail to poisons and occasion-

TABLE 58(a)
APPROXIMATE OPERATING CONDITIONS WITH DIFFERENT CATALYSTS

Process	Molybdenum Catalysts				Platinum Catalysts		Other Catalysts		
	Thermal Reforming	Fixed bed	Fluidised bed	Moving bed	Non-regenerative	regenerative	Thermo-	Cyclo-	version
Catalyst composition	None	10% MoC ₃ on Al ₂ O ₃	10% MoO ₃ on alumina	Cobalt molybdate	Pt and halogen on Al ₂ O ₃ max 0.3% pt	0.5 to 0.8% Pt on Al ₂ O ₃	Cr ₂ O ₃ on Al ₂ O ₃	Bauxite	
Capacity of catalyst (life)		about 10 months	10 bbls per Kg		300 bbls per Kg	300 bbls per Kg	5 bbls per Kg	—	
Reaction conditions (T°C)	500—600	500—580	480—560	475	450—500	450—510	500—530	500—580	
Pressure (atmos)	20—75	10—20	10—25	25—30	20—50	20—30	10—20	2—10	
Space velocity (1/m)		0—5	0.3—1.0	1.0	1.0	1—5	0.7	1—7	
Contact time sec	10—20	15							
Gas circulation H ₂ : oil mole ratio.				0—5					

ally contribute adverse reactions like ring opening. Houdri forming process employs platinum catalyst in fixed bed reactors, while plat-forming may be conducted in semi-regenerator or cyclic regenerator reactors. Cyclic regeneration is periodical and is required at an interval of 24 to 48 hrs. During this regeneration time, a spare reactor is switched into stream; thus three reactors will be on stream while the fourth one will be in regeneration. Continuous Houdri forming¹⁰ reactions are conducted on bimetallic catalysts, platinum and rhenium compositions. These catalysts are able to resist coke formation. Semi-regeneration requires a long time before regeneration is attempted, usually a time of 3 to 6 months operation renders the catalyst ineffective

5.3.2.1 Feed stock selection

Reforming helps in boosting octane value by converting most of the *n*-paraffins to aromatics. Hence this process can be applied to produce aromatics. Stocks that are suitable for gasoline engines are chosen as the feed material for reformer and straight run gasolines of low octane number mainly constitute the bulk of feed. Light products obtained in various cracking operations in gasoline range are also suitable. The feed stocks in gasoline-range have the boiling point spread from 35 to 180°C. Upto C₆ carbon atom (i.e. 35 to 78°C) the fraction by its nature possesses good octane value and further attempt to improve octane number is not worthy. In fact this fraction enjoys a free ride in the reactor at the prevailing conditions. A minimum of six carbon atoms is essential for production of simplest aromatic ring. So, depending upon the highest aromatic compound (usually xylene), the carbon atoms range in the feed may be fixed. In other words, for production of benzene, toluene, xylene, six to eight carbon atoms must be present in the feed. Virgin or cracked gasolines, invariably contain impurities like sulfur, nitrogen and oxygen compounds, and their presence is more if crude is naphthenic. Feed stocks for reformers must be free from these compounds, preferably sulfur^{11-a} and nitrogen compounds should be kept as low as 5 ppm. Hydrodesulfurisation of feed stock assures the required purity. Sulfur removal not only helps in reducing corrosion, but also coke deposition. Specially

for platinum catalysts, feed stocks should not contain more than 5 ppm of nitrogen and 10 ppm of sulfur.

5.3.2.2 *Operation with different catalysts*

About 90% reforming operations are conducted in fixed beds using platinum catalysts. Moving beds and fluidised beds mainly use cheap catalysts of molybdenum and chromium compositions. Fluid hydroformers¹² employ catalyst molybdena on alumina. Thermoform Cat. forming¹¹ is done in moving beds using chromia on alumina as catalysts. These catalysts greatly help in removing sulfur to almost zero presence, followed by low yields of butane. The temperature can go up to 525°C. Bauxite and clays have also been utilised as catalysts, but at present much significance is not attached to these catalysts. One difference between these clay catalysts and platinum catalysts is in the production of hydrogen. Not much hydrogen is produced with clay¹⁴ catalysts hence none of the products is recycled. Usually in cat. forming operations¹⁵ 70 to 350 M³ of hydrogen per cubic meter of feed stock is produced. Platinum combinations have been found to yield less light ends, (propane butane and pentane) compared to conventional platinum catalysts. It is interesting to note that the yields of these components is linear and inversely dependent upon the yields of reformat. Usually the total amount of such light ends produced in reforming operations (platinum catalysts) falls from 15 to 5% while reformat yields increase from 75 to 95%.

A correlation presented, by R. R. Jacob^{11b} is very interesting, on the yields of potential aromatics (A_p) in reforming operations, which is given as

$$A_p = \left(\begin{smallmatrix} 0.875 \\ \rho \end{smallmatrix} \right) (0.85 N + A)$$

where,

N = % volume of naphthenes in feed

A = % volume of aromatics in feed

ρ = specific gravity of feed at 15.6°C

At lower pressures increased yields of aromatics and hydrogen are experienced.

5.3.2.3 *Catalytic Reforming (Platforming)*

Catalytic reforming process employs platinum and other combinations as catalysts. Hydrotreated naphtha (68-180°C) is mixed with recycle hydrogen and sent through a furnace. The outlet temperature of the vapours shall be around 500°C. Hot vapour is sent into three catalyst cases (reactors) in series. Old designs may enjoy four reactors in series: the last one is known as swing reactor. Swing reactor comes into main stream when regeneration is attempted. Pressure in reactors is kept in the range of 15 to 75 atmos. Except hydrogenation reactions, which are less prevailing, all other reactions require heat, this invites a heater to substantiate heat of reactions and is placed in between two reactors. Cyclisation reactions are pronounced at severe conditions, hence the last reactor operates generally at higher temperature by 20 to 30°C from the preceding one. Catalysts are made into pellets of 3 mm size. Halogenation is prescribed whenever regeneration is carried out. The operation is shown in Fig. 5.11(a). After the reforming is over, the effluents are cooled and gas is separated. High pressure separator removes recycle gases mainly hydrogen, while low pressure separators relieve most of the light fractions. Hydrogen is usually produced to an extent of 2.5% by weight of feed. High recycling ratios prevent coke deposition and the space velocity is kept below 2 in all these operations. In regenerative processes, the space velocity goes upto 5. Continuous operation as developed by UOP is classified as platforming operation, and is presented in Fig. 5.11(b). As the name suggests, continuous regeneration of catalyst is achieved here. Further, continuous rates and constant quality production of reformat of high octane value and production of LPG from naphthas are some remarkable advantages in this system.

Arrangement of three stacked reactors one over the other forms the main difference in reactor arrangement. Feed and catalyst travel cocurrently in all these reactors from top to bottom. Heating the reactants in between the reactors remains unchanged. The catalyst from the bottom of the third reactor is transferred to separate regenerator. After regeneration the catalyst is transferred to the first reactor continuously.

Englehard Magnoforming employs platinum on bimetallic catalysts. The rugged nature of the bimetallic catalysts permit

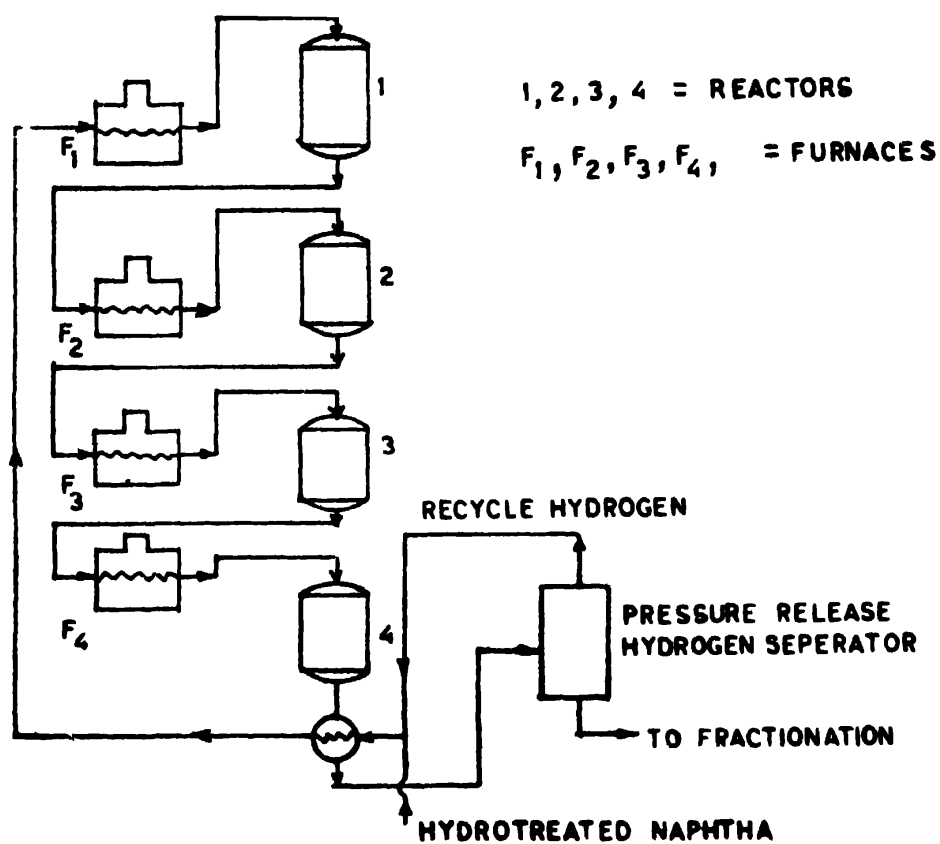


Fig 5.11(a) Catalytic Reforming

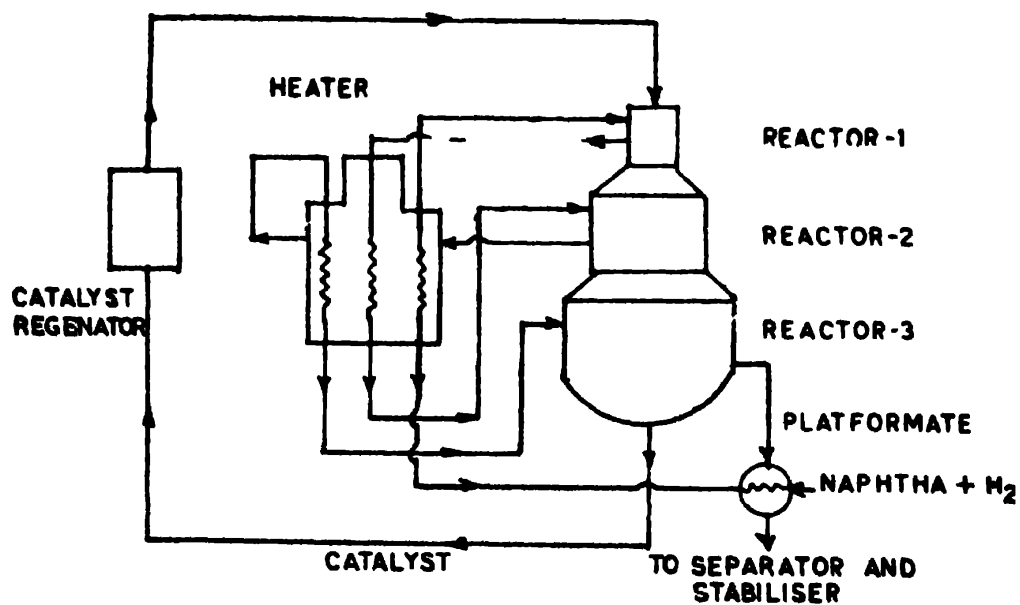


Fig 5.11(b) Plat forming

the operation to be conducted at much severe conditions and also tolerate sulfur up to 20 ppm.¹⁶ Institut Francais due Petrole has formulated number of catalysts of different platinum contents, to reduce the cost of catalyst and at the same time permitting the operation at much severe conditions. Also, these catalysts can work actively under pressures less then 20 atmos. This leaves an advantage to the operators in choosing low pressure or high pressure or combination of these two depending upon the necessity.

5.3.2.4 *Iso plus Houdri Forming*

This is a combination process, laces cat reforming with thermal reforming. In another combination reformat extraction plant is provided to remove aromatics, as this helps in recycling paraffins rich raffinate. This process instils the polymerisation unit for C_1 and C_2 off gases. No drastic pretreatment of feed is essential as the feed first goes through a guard case that helps in removal of sulfur and nitrogen impurities. After guard case, the feed passes through an array of reactors and Houdri reformat is obtained as an effluent from the last one and directed to other combination units. Different types of combinations are shown in Fig. 5.11. (c).

The system lends and adjusts itself for regeneration when operating at high severities. Polymerisation of the off gases helps in obtaining quantity and quality gasoline. Conversions up to 80% of naphtha are possible yielding an octane value of 108.

Operating conditions :

Temperature	470 - 540°C
Pressure	10 to 50 atmos
Sp. velocity	1.5 to 5.0 V/hr. V
Hydrogen to oil ratio	3 to 10 (vol basis)

5.3.2.5 *Rhein Forming*

This is a fixed bed regenerative process. Rhenium-platinum combinations are quite good in resisting fouling. These can be operated at pressures below 20 atmos. High space velocity with lower recycle ratios of hydrogen (3 to 3.5) are permissible. At low pressure operations, increase in quantities of aromatics and

hydrogen is experienced. Rheinforming was first used by Standard of California in 1967 and is getting popular.

Yields are approximately 75% to 84%.

Octane number of reformat is approximately 100.

Hydrogen yield per barrel of feed 50 to 60 M³

C₁ to C₄ fractions per bbl. : 10 to 12 M³

Outlet pressure of reactors : 10 to 15 atmos.

Universal Oil Products⁴⁷ Co have also developed catalysts consisting of Platinum - Rhenium and Selenium for reforming operations.

5.3.2.6 *Power forming*

Power forming process may be designed to operate in cyclic or semi regenerative unit. Reformates of octane value 85 to 102⁺ are common. In cyclic regenerative process, any reactor can be isolated from the main system for regeneration. Thus one swing reactor, three process reactors are always in service. Platinum and multimetal catalysts are used in cyclic operations. A novel metallic catalyst KN-130 is found to be superior in semi-regenerative operation because it maintains the activity to a high degree compared to the previous platinum combinations. Three percent yield of hydrogen and 11 to 17% yield of C₁-C₄ fraction is a notable thing.

5.3.2.7 *Selectoforming*

Selectoforming⁴⁸ is a mild hydrogenation process. Non-noble metals act as catalysts; activators like potassium enhances the capacity of catalysts. These are zeolite based dual functional catalysts, and distinguish themselves from other catalysts in permitting only straight chain compounds to react. Achievement in quality of octane number is significant. Low volatility gasoline is obtained as main product. The life of catalyst is very long.

Operating conditions :

Temp.	350 to 500°C
Pressure	5 to 40 atmos.
Sp. velocity	1—10 V/hr. V.
H ₂ : oil	1—12 (Vol.)

The salient observations made available are

Increase in C_5^+ product with increase in octane number

Increase in propane yields (7 to 9% at 95 to 100 octane number range)

Aromatic content of reformate is reduced, if octane no. increases.

50% to 60% aromatic production is reduced if octane value is to be in the range of 95 to 100.

Front end volatility is reduced.

5.3.2.8 *Ultraforming*

This process is specially designed for low pressure operations with regenerative catalysts. As the composition of noble metal in these catalysts is very small, they are very rugged and active too. The catalysts are exceptionally good for high temperature operations (600°C) and possess characteristically long life.

The effect of pressure⁹ can be revealed by observing Table 5.8(b).

TABLE 5.8(b)

	Pressure and yields in reforming			
	High 30 atmos	Medium 24 atmos	Medium 17 atm	Low 10 atm
H ₂ yield wt%	22	25	28	30
C ₅ ⁺	81.6	83.4	84.9	86
First cycle lengths months	14	12	9.5	5
Hydrogen purity %	80	83	86	87

Reduction in operating pressure immensely decreases the operation time, though light fractions are produced more in quantity and quality.

5.3.2.9 *Reforming*

This employs a catalyst of platinum irridium and palladium deposited on inert base. Developed by Exxon Research and Engg. Co., the catalyst is credited with outstanding activity and

high yields of C_5^+ products. This process can be used in combination with platforming operations and simultaneous extraction of aromatics.

Approximate heats of reactions in different processes are shown in Table 5.8(c).

TABLE 5.8(c)

Approximate Heats of reactions

<i>Process description</i>	<i>Heat of reaction kJ/Kg</i>
1 Low pressure vapour phase thermal cracking	169.95
2 Vapour phase thermal cracking (gas oil)	156.69
3 Mixed phase thermal cracking	124.44
4 Mixed phase thermal cracking of light gas oil	113.27
5 Thermal reforming naphtha	101.44
6 Catalytic cracking heavy gas oil	88.68
7 Catalytic cracking light gas oil	78.24
8 Catalytic reforming of naphtha	69.89

Problem 5.2

A virgin naphtha (800–100°C) has been reformed over platinum catalyst. Three reactors are in series to achieve a clear RON 97 reformate. The reformer capacity is 10,000 BPSD. From the data given below :

- Estimate losses
- Find net Hydrogen
- Present complete material balance
- Find the amount of catalyst in each reactor

Data

<i>Properties of feed</i>		<i>Properties of reformate</i>
BP—80 to 110°C		50 to 110°C
Average mol. weight 90		85
Characterisation factor	11.59	11.52
API	50.2	
Sp.gr.	0.7781	0.782
S%	0.01	0.0004

Space velocity 3
 (V/V. hr) Liquid
 Reactor conditions
 Pressure 20 atmos.
 Temperature 45°C
 Bulk density of
 catalyst 0.82

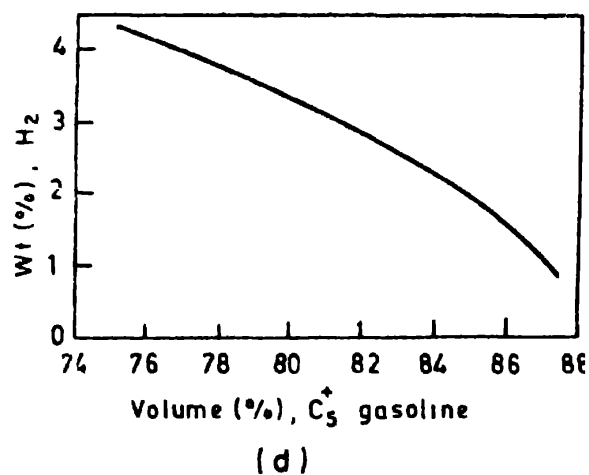
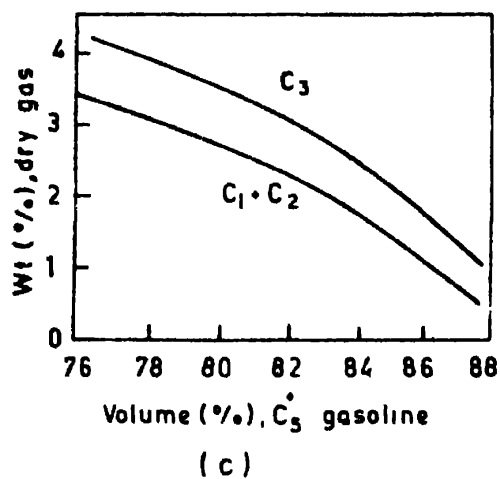
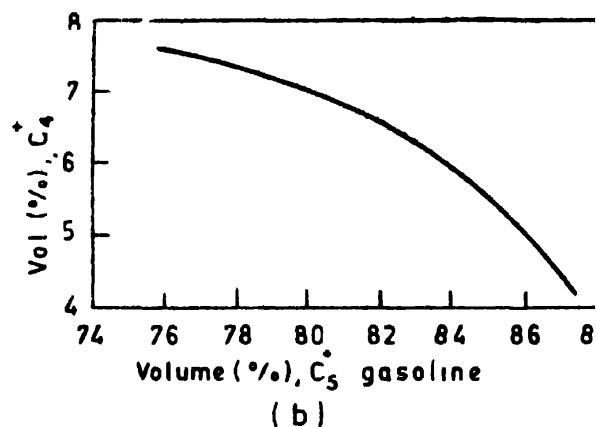
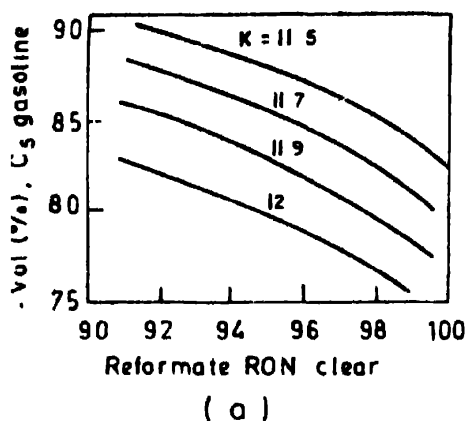


FIG 512 Approximate yields of H₂, gases and gasoline in reforming unit

- (a) Octane number Vs C₅ yield
- (b) Vol % C₄ fraction yield Vs Vol. of gasoline
- (c) Dry gas Vs gasoline yield
- (d) H₂ yield Vs. gasoline yield

Solution

From Fig. 5.12(a) Vol. of gasoline ($> C_3$) at $K = 11.59$ and
97 Octane no $= 87\%$

5.12(b) Vol. of C_4 fraction at 87%
gasoline $= 4.4\%$

5.12(c) Weight of dry gas at 87%
gasoline $= 2.2\%$

5.12(d) Weight of H_2 $= 1.3\%$

$$\begin{aligned}\text{Feed in Kgs/day} &= 10,000 \times 200 \times 0.7786 \\ &= 15,57,200\end{aligned}$$

$$\begin{aligned}\text{Reformate} &= 15,57,200 \times \frac{0.87 \times 0.782}{0.7786} \\ &= 13,60,680 \text{ Kgs/day}\end{aligned}$$

Sulfur balance

$$\text{Sulfur in feed} = 15,57,200 \times \frac{0.01}{100} = 155.72 \text{ Kgs/day}$$

$$\text{Sulfur in product} = \frac{13,60,680 \times 0.0004}{100} = 5.44 \text{ Kgs/day}$$

$$\text{Sulfur in } H_2S \text{ (balance)} = 150.28 \text{ Kgs/day}$$

$$\text{Net Hydrogen} = \text{Total hydrogen produced} - \text{Hydrogen in } H_2S$$

$$\text{Hydrogen in } H_2S = \frac{2}{32} \times 150.28 = 9.40 \text{ Kgs/day}$$

$$H_2 \text{ produced} = \frac{15,57,200 \times 1.3}{100} = 20243.6 \text{ Kgs/day}$$

$$\text{Net Hydrogen} = 20243.6 - 9.40 = 20239.2 \text{ Kgs/day}$$

$$\text{Dry gas} = \frac{2.2 \times 15,57,200}{100} = 34258.4 \text{ Kg/day}$$

$$C_4 = \frac{10,000 \times 200}{22.4 \times 100} \times \frac{4.4 \times 58}{1000} = 227.85 \text{ Kgs/day}$$

(where 58 is the mole weight of C_4 fraction)

Losses :	Reformate	=	13,60,680
	H_2S	=	150.28
	Net H_2	=	20,239.2
	Dry Gas	=	34,258.4
	C_4	=	227.85

$$\text{Total} = 1,41,645 \text{ Kg/day.}$$

Losses : Feed-Total = 1,41,645 Kg/day (High,
because of graphical errors).

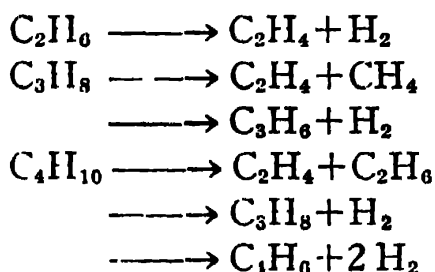
Catalyst volume : (at '3' hourly liquid space velocity)

$$\frac{10,000 \times 200}{24 \times 3 \times 1000} = 27.8 \text{ cu. Meters.}$$

5.4 Naphtha Cracking

In almost all parts of the world, naphtha cracking is appropriated to produce olefins, mainly ethylene and propylene. In fact any petroleum stock is suitable and is in a position to replace naphtha, which is preferentially reserved for steam reforming process.

Alternatively olefins and diolefins can be produced by dehydrogenation of paraffins of suitable range. As an example, propane and ethane can be cracked/dehydrogenated to yield corresponding olefins as given by the following reactions :



Dehydrogenation reactions are quite fast, hence it is wise to choose the feed stock (mole.weight) as close as possible to the required olefin. The following Table 5.8(d) furnishes the yields of ethylene while cracking different feed stocks⁴⁰.

TABLE 58(d)

Ethylene yield

Charge Stock	Cracking Temp. °C	Yield %
Ethane	810	40—70
Ethane + Propane	800	40—70
Naphtha (EP 200°C)	745	37
Gas Oil (EP 420°C)	680	20—28

For cracking lighter stocks the temperature of cracking has to be increased.

Table 5.8(e) shows the yields of different products by cracking naphtha.

TABLE 5.8(e)
Naphtha Cracking & Yields

	Low severity yield %	--	High severity (%)	Naphtha cracking + Conversion of % C ₃ & C ₄ fractions
CH ₄ & lighter	13.6		20.8%	16—22%
C ₂ H ₄	26		36.4	34.9—42.7
C ₃ H ₆	17.5		12.6	—
C ₃ H ₈	1.2		1.0	—
C ₄ H ₈	12.6		9.0	—
C ₅	29.1		21.1	32 to 23

When ethane and propane are chosen as feed stocks, the following points must be pondered.

Methane : It enjoys a free ride in the reactor hence it increases the burden in the system.

Propane and Butanes : Both produce olefins of same carbon atom range in the beginning ; for alkylation and polymer gasoline these can be used comfortably.

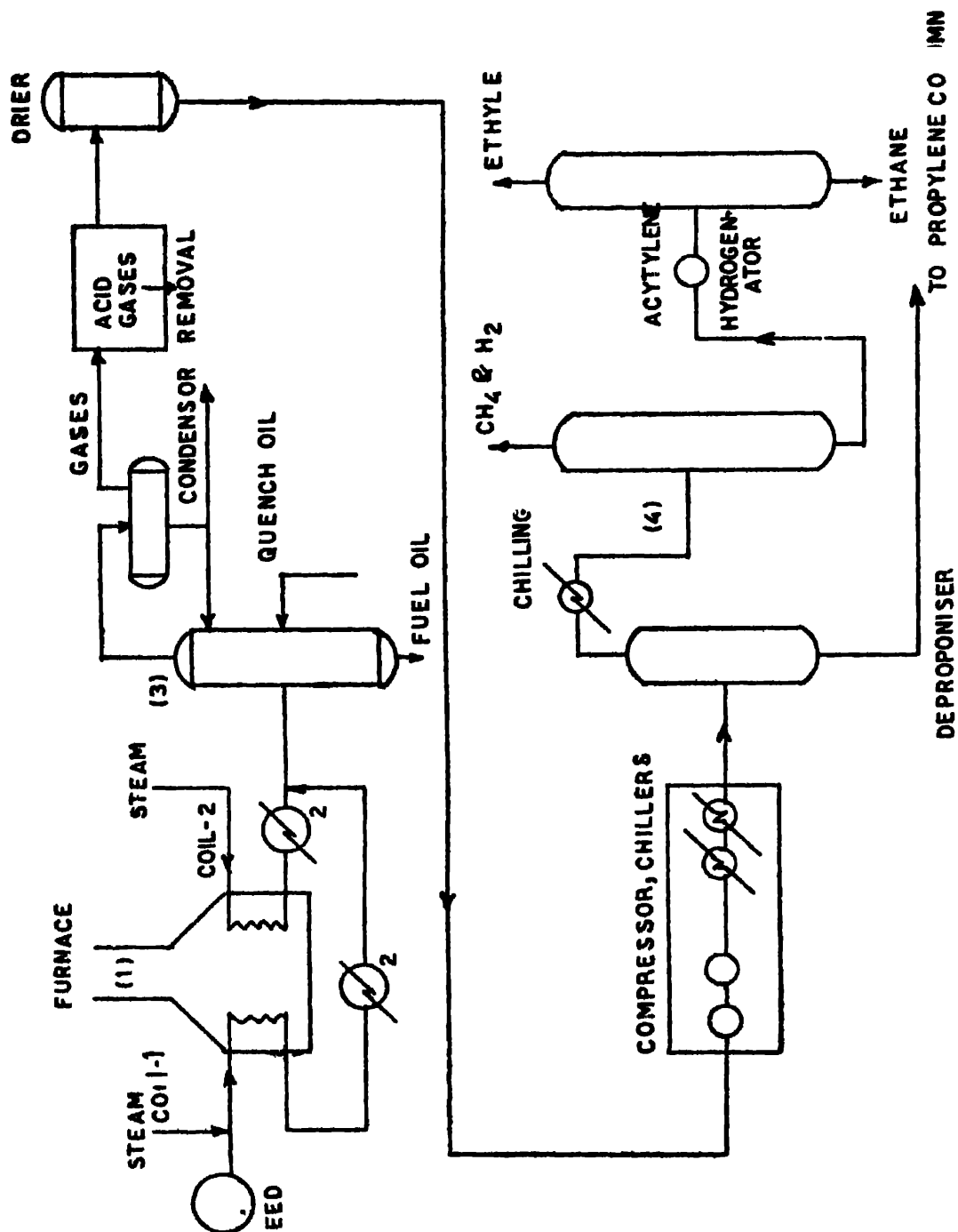
Carbondioxide : This is always present up to 20 ppm. in all cracked stocks. It should be removed before the feed is cracked.

Hydrogen Sulphide : Mostly present in all feed stocks ; one way it is beneficial, as it inhibits coke formation.

Oxygen : It is a dangerous component as it leads to explosion.

Nitrogen and other inerts : No problem.

Naphtha cracking for olefines is schematically presented in Fig. 5.13. The hydrocarbon feed stock is preheated and cracked in presence of steam in a tubular furnace (1) (Lumus employs a short residence time (SRT) cracking furnace, while Kellogg Co. achieves a high flexibility in a furnace containing entirely separate pyrolysis radiant section). The furnace is maintained at a high temperature, such that the effluents record a temperature of 800 to 850°C. as soon as the furnace effluents emerge out of furnace,



they are cooled in a transfer line heat exchanger (2), which is set apart for production of high pressure steam (100-120 Kg/cm²). Still hot, the products are rapidly quenched by showering with feed stock or with circulating oils. Direct quenching with water is also practised in some cases (Braun & Co). Quenching with oils is done in a pyrolysis fractionator (3), where fractionation is also carried out simultaneously. The bottom product of this fractionator shall be heavy oils or fuel oils; mostly polymer products. The lighter fractions are cooled in a reflux condenser, at the top of the fractionator. In the reflux condenser, separation of gaseous products from light distillates takes place. The gases are always infested with acidic constituents like CO₂, CO, H₂S, SO₂, oxides of nitrogen etc, and these are stripped off by suitable solvents. The acid free gases are now cooled and compressed to a pressure of 30 to 40 atmospheres where by propane and higher components are liquified. The mixture is separated into propane and gases in depropaniser unit. The top gases of depropaniser mainly contain uncondensables such as H₂, CH₄ and C₂ fractions. Further chilling will liquify C₂ fractions, from where CH₄ and H₂ streams can be easily driven off; this is done in demethaniser (4). The demethaniser bottoms are given mild hydrogen treatment to convert acetylene, which is always present in cracking operations (max. 1%) into ethylene. Ethane-ethylene fractionation is done in a column (5). Propane, from depropaniser is again processed for propane, propylene and butane fractions. Ethane and propane are again routed through furnace, but through a second coil operating at much severer conditions than the other coil. The effluents are later joined with the main stream products.

Proper selection of cracking conditions and rapid quenching achieve high yields of desired olefins, and failure of proper selection results in undesirable coproducts like methane and polymers.

5.4.1 FEED STOCK SELECTION

The lower boiling range naphthas usually contain more hydrogen, hence the products after cracking also follow the same pattern; with increasing partial pressure of cracking stock, the amount of hydrogen produced falls down. Most frequently the amount of hydrogen available in cracked products vary from 10 to 16% for heavy residuums to light naphtha. Significantly for

the same feed stock when operating at high partial pressure (1.2 kg/cm^2) then the amount of hydrogen drops down to 9%, while the same feed operating at 0.3 kg/cm^2 contributes as high as 15% hydrogen.

Aromatic rich stocks offer more resistance to cracking, hence their presence always detracts the efficiency.

Naphthenes pyrolysis proceed by dehydrogenation, ultimately lead to more aromatic and hydrogen concentration. Paraffins, the left out series, are naturally preferred sources, although *n*-paraffins are better than *i*-paraffins.

5.4.2 EFFECT OF STEAM

The function of steam is to reduce hydrocarbon partial pressure. The effect of partial pressure is shown in the Table 5.8(g). In coking systems, cracking pressure will be kept always below 3 kg/cm^2 . The addition of steam by 0.4 to 1.0 times the weight of oil, shall effectively provide the partial pressure required for the system.

The function of steam is to reduce the partial pressure of hydrocarbon. In fact most of the naphtha crackers are operated at normal pressures, however it is closely dependent upon the boiling range of feed stock.

By increasing partial pressure of hydrocarbon, an increased coke deposition is obvious. Steiner emphasised the importance of steam in such cracking reactions, the quantity of steam is exceptionally governed by the molecular weight of feed stock operating pressure as shown in the Table 5.8(g).⁴¹

TABLE 5.8(g)

Approximate yields of ethylene from naphtha cracking as a function of partial pressure of Hydrocarbon in cracking zone

O.l partial pressure Kg/cm ²	Wt. % yield ethylene		
	Light naphtha < 90°C	Medium naphtha 50—160°C	Heavy naphtha 90—210°C
0.1—0.13	27	25	23
0.4—0.62	23	19.0	17.5
1.2	16	—	—

Operating Conditions

Naphtha oil temperature	800—850°C
Ethane-Propane oil temp.	820—870°C
Steam : HC ratio	0.4 to 1. (wt)
Velocity of naphtha vapors	30 M/sec.

5.5 Coking

Petroleum coke is obtained in petroleum industry as an ultimate product of prolonged thermal cracking. It is a peerless raw material for electrodes. In fact demand for coke in electrochemical and electrometallurgical industries is immense. Furnace linings in ferrous and non-ferrous industries are yet another application of petroleum coke. Indian petroleum⁴² coke is the best in the world, due to less sulphur content in the parent material. Major benefactor of this coke is undoubtedly the aluminium industry.

At present petroleum⁴³ coke production in India stands at 152,000 tons per year. Coke producing plants and the annual turn over is presented in Table 5.9.

TABLE 5.9
COKING PLANTS IN INDIA⁴⁹

Raw coke :	
Assam Oil Company	16,000 tons/year
Barauni Refinery	78,000 "
Gauhati Refinery	36,000 "
Coke Calcining Plants approved by Govt.	
Manali	50,000 tons/year
Visakhapatnam	50,000 "
Marogo	50,000 "
Haldia	50,000 "
Bongaigaon	30,000 "
India-Carbon Ltd at Noonmati (1961)	65,000 (installed capacity)
(Raw coke obtained from Digboi, Gauhati (Anthracite coal also)	
Anthracite coal calcining plant	
Budge-Budge (1970)	12,000 tons/year
Actual production (1972-73)	58,701 "
IOC-Plant, Barauni, capacity (1971) Production	60,000 "
	40,000 tons/year
Goa Carbon Ltd., Panjim (1967)	50,000 (Capacity)

Coking is a thermal cracking operation falling in a temperature range of 500 to 650°C. Feed stocks otherwise not suitable to operations like thermal or catalytic cracking, are usually fed to coking units. Coking is influenced by the gravity and molecular structure of the feed. Propensity of cracking is an outright function of Conradson carbon residue (CCR). Industrially a concise analogical term Conradson Decarbonising Efficiency (CDE) is more familiar ; it is given as

$$\text{CDE} = \frac{\text{Carbon residue in feed stock} - \text{carbon residue in liquid products}}{\text{Carbon residue in feed stock.}}$$

Estimation of coke yields can be done by the correlations available in literature. Such correlations are linked with CCR of feed stock.

	Delayed coker	Fluid coker
44,45		
Coke yield wt %	$2.0 + 1.66 K$	$1.15 K$
Gas yield		
during coking (wt %)	$5.5 + 1.76 K$	$5 + 1.3 K$
Where K is Conradson carbon residue of feed stock (Fig. 5 15.)		

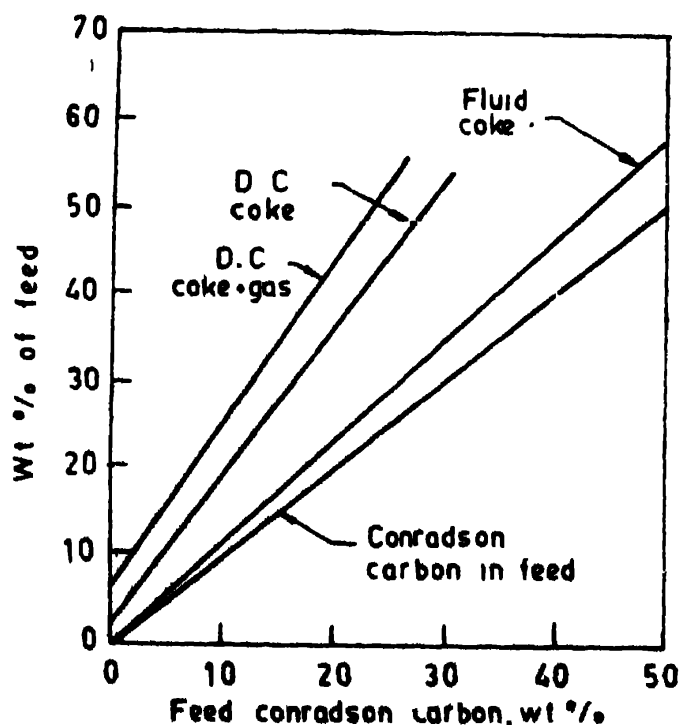


FIG. 5.15. Coke yield Vs. Conradson Carbon Residue

Aromatics, asphaltenes are desirable feed stocks for a good yield of coke. Sulfur in the feed stock though it increases coke yields, it forms an inseparable complex with coke. Once coking is complete, the removal of sulfur from such product is rather impossible; calcination of coke again strengthens the bonds between sulfur and carbon.

Sulfur crude bottoms¹⁶ and coal tar pitches are successfully blended for getting electrode coke of comparable quality obtained from asphaltic feeds.

General methods of petroleum coke production are listed below :

1. Hot oven method (Koppers)
2. Thermal cracking (two coil—Dubb's)
3. Delayed coking
4. Fluid coking
5. Contact coking.

Hot oven method

Presently, this method has no reputation in petroleum industry. With some modification the by-product coke oven batteries were employed for coking petroleum stocks. High molecular weight stocks, asphaltenes, tars, pitches serve as raw materials to these ovens. The conditions of coking are similar to metallurgical coke production. Temperature in the range of 1000—1200°C is required and coking time of 18 hours is most desirable. With pitch of CCR value 50%, coke yield shall be approximately 70%. With ample and avid modern technology in hand, this has become an unwanted process.

Thermal cracking

Thermal cracking operations and coking operations can be conveniently and simultaneously carried out by Dubb's two coil cracking technique. In cracking practice heavy oil is separately cracked and the products are mixed and chilled with fresh feed. Instead of this, the cracked products are allowed to complete cracking in evaporators. After evaporators there are flash chambers where the separation of volatiles and recycle oils take place. These flash chambers in Dubb's cracking unit are exchanged for coke chambers, where coking takes place. The small

difference can simultaneously yield cracking oils and coke too. Lighter products evaporate and escape into the fractionator. The coking operation is conducted at the same conditions as Dubb's cracking. Coke from the evaporator is later removed by any convenient technique. The off gases from the evaporator are opulent in unsaturated components.

5.5.1 DELAYED COKING

This is the most important process of all the coking techniques. In India, all plants operate on this technology only. Delayed coking is a technical outcome of two coil cracking process. Capability for cracking all types of feed materials including solvent extracts and simplicity of operation, have made this one as most adoptive in all refineries.

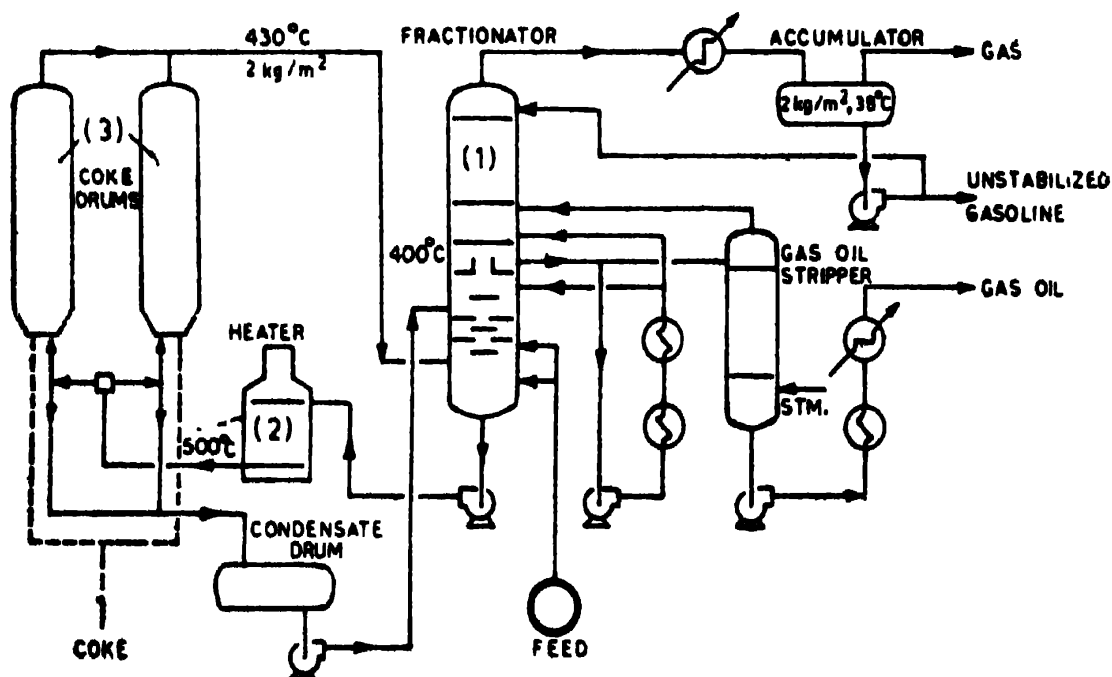


FIG. 5 14(a) Delayed coking operation

The principle behind delayed coking operation, is : heating is done in a furnace to initiate cracking and the reactions are complemented in huge and tall coke drums ; hence the name delayed coking is used. As a rule a series of such coke drums will be pressed into service. While one drum is engaged in getting feed, the other drums shall be in the process of coking and decoking. This way by orderly rotation of the drums the

process may be contrived to work continuously. Minimum two drums are essential even for small capacity plants, in fact sets of drums in series are desirable. Usual operating conditions in delayed coker are given below :

Operating conditions

Heavy oil, discharge temperature	470—520°C
Coking temperature	450—470°C
Pressure in coke drums	5 to 6 atmos
Drums diameter	4 to 5 M
Height	14 to 20 M
Thickness of drum	about 4 cms.

Recycle ratios of fresh (heavy) and light oils are adjusted to maximise yields of either liquid or solid products. An yield of 30% coke for reduced crudes or 80% for tars and pitches may be expected. Coke from these units contains volatile matter upto 8-15% and the bulk density may be around 9 kgs per liter. CDE of the plant may be reaching upto 99.8%.

Conventional delayed coking process is shown in the flow diagram (Fig. 5.14a). The process begins with the fresh feed entering the fractionator (1) The fractionator complys with all the assigned duties as in two coil cracking plant. Heavy oil from the bottom of fractionator passes through a heater (2) at

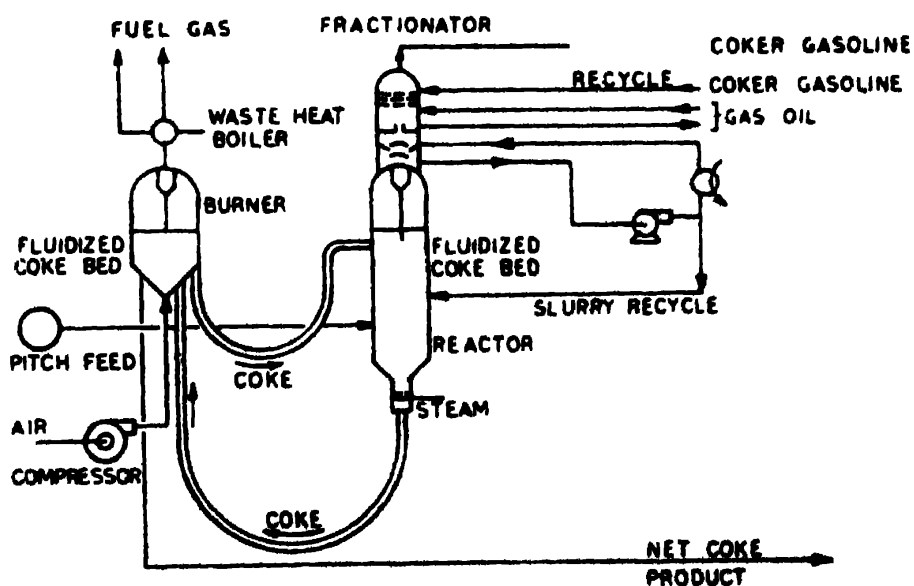


FIG. 5.14(b) Fluid coking

a high velocity. Introduction of steam into heating coil prevents coke deposition in coil. The hot and partially vaporised mixture enters the coke drum (3). The coke drum is charged with hot mixture to half to two-third of the height of the drum ; or to a convenient marked level.

The level of hot mix in drums is modulated by cathode ray monitoring. Steam and volatiles escape from the coke drums and enter the fractionator. This fractionator is also known as dephlegmator. These vapours preferentially relinquish heat to incoming feed ; and in this act stripping of volatiles from feed takes place.

Changing of coke drums may require a time of 4 to 5 hours. Immediately after changing is over the drum shall be isolated from the stream. Effluents of the heater shall now be switched in to second drum. Coking being slow usually takes a time of 10 to 16 hours. Time of charging coke drums must balance the time of coking and decoking operations.

Rough estimates of coke formed in drums is possible if calibration of drums (tons per centimeter height) is done.

5.5.1.1. *Decoking*

Coke being set and hard, much difficulty is encountered in removing coke. Decoking is a time consuming and arduous task. Lot of developments took place in the direction of decoking operations. Presently hydraulic jets at 150 to 200 atmospheres pressure are directed to break the coke, in place of once used mechanical breaking with hammers, an orthodox way still prevailing in some countries that offer cheap labour. Drilling and mild dynamiting is also allowed. Of late the ingenious chain pulling technique has been acclaimed and welcomed by the industry. The technique consists of suspending strong chains in coke drums from the hooks fixed to the thick shell of drum at the top. Other ends of the chains are free to fold and lie submerged under charge. After coking is over, usually steaming is done to drive off hydrocarbon vapours. The top flange is disconnected and the chains are pulled by cranes ; this upward thrust shatters the coke to pieces, making easy for coke removal. Influence of feed stocks properties on coke yields are shown in Table 5.10a, b & c.

TABLE 5.10(a)

EFFECT OF API GRAVITY ON DELAYED COCKER YIELDS			
CARBON RESIDUE	16%	16%	16%
Coking conditions			
Drum outlet temp °C	435	435	435
Drum pressure kg/cm ²	1	1	1
Charge API	12.3	13.0	14.0
Product yields wt%			
Gas (Vol%)	4.2	4.0	3.6
Coke	16.6	15.5	13.6
Gasoline	8.9	8.8	8.6
Gas Oil	19.0	17.3	19.1
Heavy Gas Oil	53.3	54.4	55.1

TABLE 5.10(b)

COMPARISON OF DELAYED COKING AND FLUID COKING

Charge—	Delayed	Fluid
Gravity °API	15	15
Conradson Carbon		
Residue	9	9
Sulphur	1.2	1.2
C ₈ and Lighter	6.0	5.5
Coke	22.0	11.0
CDE%	99.8	91.2
Charge—	Contact Coking	Delayed Coking
Gravity	18.9	18.9
Conradson Carbon	11.7	11.7
Sulphur	0.6	0.6
Products		
Lighter fractions %	14.9	7.5
Coke %	13.0	20.0
CDE %	99.3	99.3

TABLE 5 10(c)
EFFECT OF RECYCLE RATIO

Recycle ratio vol %	0	20	40
Product yields			
Coke	15.5	18.0	20.0
Gas	4.0	5.5	6.0
Gasoline	13.0	15.0	15.5
Gas oil	21.5	26.0	28.5
Heavy Gas Oil	46.0	36.0	24.5

5.5.2 FLUID COKING

Search for continuous coking has inducted the concepts of fluidisation with necessary modifications. Fluid cat. crackers use catalysts to bring the cracking and here cracking and coking are catalysed by coke particles. Explicitly, it is nothing but formation of excessive coke on surface of particles; as a special case these happen to be coke particles. Coke particles produced in the same unit assume more or less spherical shape and act as heat carriers while travelling from burner (regenerator) to reactor, and coke carriers in reverse travel. Some portion of steam stripped coke is burnt and the remaining coke is taken out. The hot coke particles are in a state of fluidisation caused by incoming vapours. Thus the effective continuous circulation of coke seeds namely coke particles is unavoidable. A close look at Fig. 5.14(b) reveals the process sequence. About 20% of coke produced is consumed to maintain coking reaction.

Operating conditions

Reactor temperature °C	480—560
Pressure	— Normal
Burner temperature °C	590—650
Pressure (Burner)	about 2 atm.

5.5.3 FLEXICOKING

Petroleum industry, largely lured by gasification, the hub of modern petrochemical industry has given to a matrix of coking and gasification operations in the form of flexi coking. This

integration enables refineries to convert vacuum residuums, other heavy feed stocks into desulfurised liquids and gases. As a result 99% vacuum residuums end up as liquids or gases with less than one percent sulfur.

Fig. 5.14(c) shows the outlines of the process. Residuum feed is injected into reactor where thermal cracking takes place

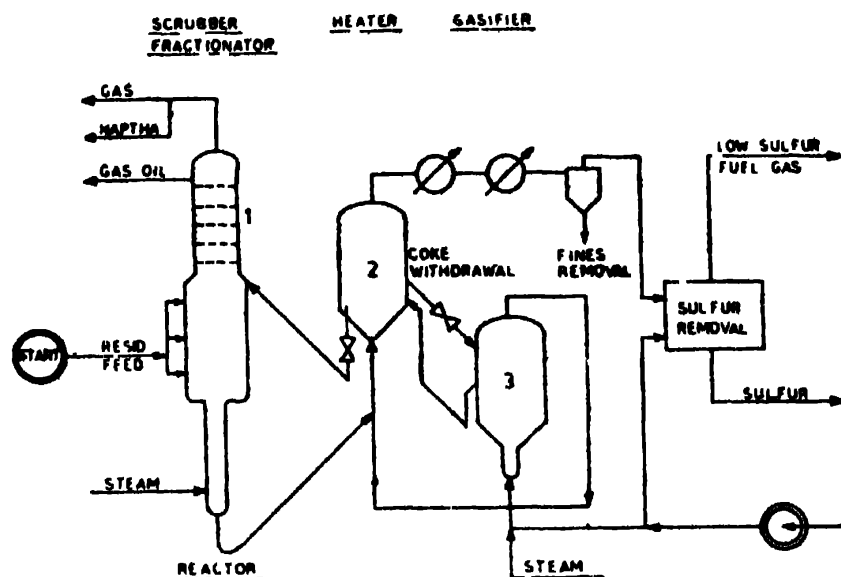


FIG 5.14(c) Flexi coking

Lighter products leave the reactor and enter the scrubber cum (1) fractionator. The purpose of fractionator is not only to rectify the volatiles, but also to entrap the coke fines leaving the reactor. Steam (admitted at the bottom of reactor) stripped coke circulates into heater (2), where devolatilisation takes place ; hydrocarbon gases obtained in this process are subsequently treated for purification. Coke formed in the heater is sent into gasifier (3), where coke is encountered with a stream of air and steam. Gasified products again join the main gas stream for purification. Part of coke may be withdrawn if necessary, at any point between heater and gasifier.

5.5.4 CONTACT COKER

This is also a continuous process. The essential steps in this process are

- (a) Oil wetted circulating coke particles are allowed to flow

downward in reactor in a dense bed. Sufficient time is provided, in this way to complete cracking, coking and drying operations.

(b) Reheater, heats the circulating coke particles to the requisite temperature levels.

(c) Coke circulation system elevates the coke particles as dense unagitated column.

(d) Fractionation system for separation of volatiles.

The operation is depicted⁴⁸ in Fig. 5.14(d). Coke circulates always between reactor and heater. A part of coke is always

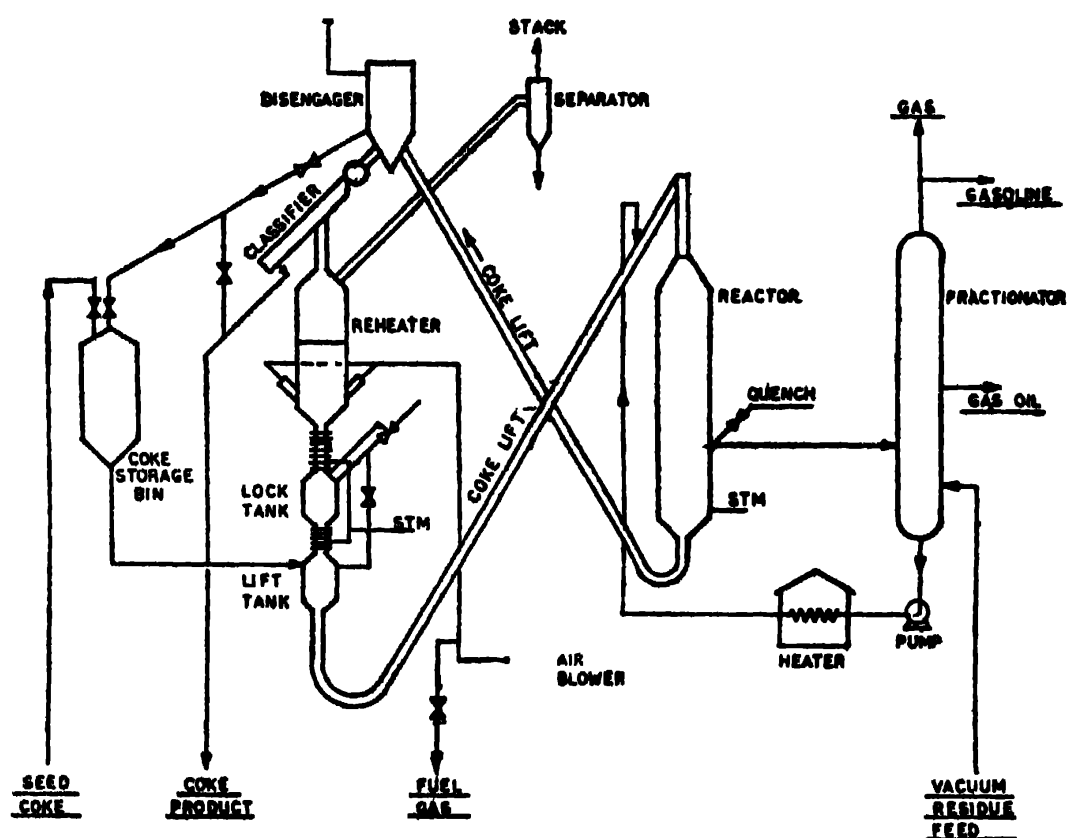


FIG. 5.14(d) Continuous contact coking

essential for supplying thermal energy and remaining portion is separated from the disengager as shown in figure.

Advantages accrue in the process, mainly in

- (a) Handling heavier residuums.
- (b) Great flexibility in operation and control.
- (c) Coke drums—cleaning is eliminated.

TABLE 511
ULTIMATE ANALYSIS AND PHYSICAL PROPERTIES OF
INDUSTRIAL CARBONS⁵⁰

	Calced petroleum coke	
	Delayed	Fluid
Carbon wt %	98.40	93.90
Hydrogen wt %	0.14	1.27
Nitrogen wt %	0.22	0.33
Oxygen wt %	0.02	0.09
Sulfur wt %	1.2	4.90
Ash wt %	0.35	0.20
Bulk density kgs/lit	0.89	0.99
Hardness Index HW	38	31
Real density gm/cc.	2.05	1.94
Specific Resistivity ohm	0.089	0.115

5.6 Hydrogen Processes

Hydrogen processes in a refinery play a vital role. The significance of these processes is increasing day by day. In 1955, these were inducted into refinery, but, due to high cost of operation, the growth was not as expected. Now with better technology in hand and reduction in cost of operation, these processes have become economic and refiners deem them as necessary.

The trends in hydro processing operations can be judged from following⁵¹ information.

	years	
Capacity of process	1955	1966
Cat. cracking	13.3%	6.9%
Reforming	0.7%	12.9%
Hydrogen	1.2%	13.5%

as indicated by Carter⁵² indicates

Thermal cracking	3.66	Million barrels per day
Cat. Cracking	8.20	" "
Hydrocracking	1.39	" "
Coking	1.80	" "

Mathias Pier⁵³, the father of hydrogenation processes, might not

have realised the importance of these. The largest hydrocracking unit at present takes up 80,000 barrels per day. This shows desirability and significance of a hydrocracker in a modern refinery.

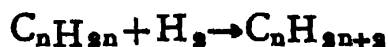
Hydrogen processes are divided into two classes as hydrocracking and hydrotreatment. These are dealt vividly in this chapter.

5.6.1 HYDRO CRACKING

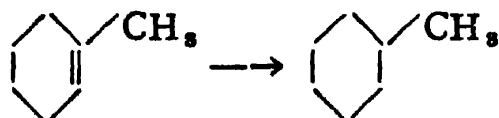
The name implies cracking in presence of hydrogen. In recent years, the tendency of hydrocracking has gained significance. While cracking (catalytic or thermal) is required to produce more light fractions from feed stocks prone to cracking, hydrocrackers take feeds of relatively refractory nature like cycle oils, coker distillates etc. Being refractory, these stocks resist cracking, but with high pressure of hydrogen they crack quite easily. In fact in a modern refinery both catalytic and hydrocracking work as a team. With improved technology it has become possible to handle even reduced crudes. Naphthenic stocks are preferred in catalytic cracking while paraffinic stocks require hydrocracking. Thus hydrocracking has become a powerful tool to the refiner in the production of quality gasoline or mid barrel products from heavy distillates or fuel oils.

5.6.1.1 *Reactions in Hydrocracking*

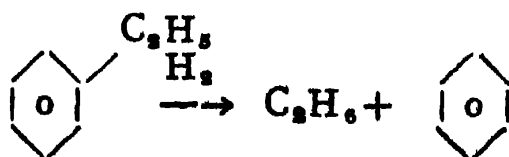
Thermal or catalytic cracking produce an olefin during cracking from a big molecule of paraffin. Hydrogen takes the charge of saturating the olefin produced as shown



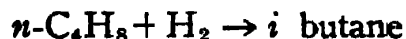
Unsaturation in straight chains as well as in ring structures is gradually eliminated.



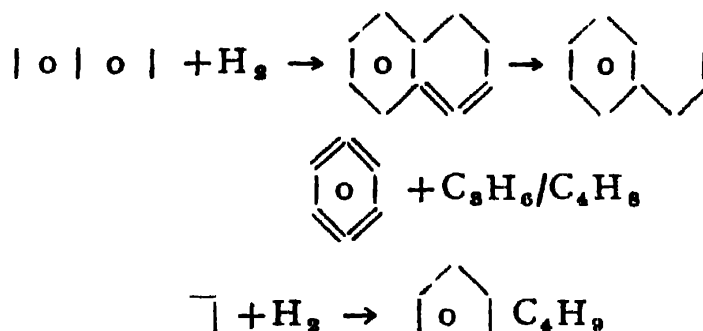
Detachment of side chains and isomerisation reaction are very frequent with ring structures.



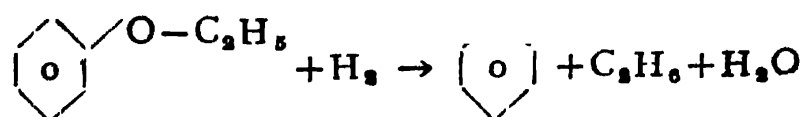
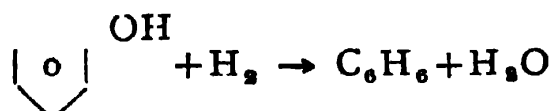
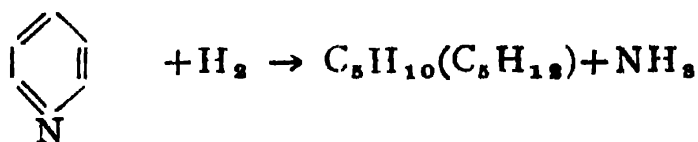
Isomerisation takes place in all types of components



Cracking of naphthalene gives the following products⁵⁴



Supplementary reactions are some elimination reactions. Compounds of N₂, S, O₂ are converted to corresponding hydrides as listed below.



Hydrogenation reactions are exothermic, while cat. cracking reactions are endothermic. Thus hydrocracking and cat. cracking are complementary to each other; in the sense, cat. cracking provides olefins for hydrocracking; while hydrocracking produces necessary heat for cracking. If hydrocracking is more, then the reaction becomes wayward due to the huge amount of heat produced; cat. cracking even though it is endothermic cannot consume all the heat. A better method of heat removal is to quench the reactants with cold hydrogen during reaction.

Practically all amount of feed is consumed in hydrocracking, hence the yields are likely to exceed 100%. Interestingly, small amounts of light gases are produced compared to normal cat. cracking operations. Hydrocracking produces more saturated compounds, hence for quality gasoline, cat. cracking or reforming of gasolines may be necessary.

5.6.1.2 Catalysts

Reactions of hydrocracking require a dual function catalyst that can give cracking and hydrogenation activities. Cracking is due to acid sites supplied by silica-alumina or alumina, hydrogenation function is due to metals like nickel, tungsten, platinum, palladium, molybdenum. Acid sites are sensitive to basic nitrogen. Nickel (5%) wt. on silica-alumina acts as good catalyst for treated stocks, i.e. stocks possessing not more than 50 ppm of nitrogen. These catalysts can work at a temperature of 350 to 370°C and a pressure of 100 atmospheres. The effect of nitrogen can be decreased by increasing the reaction temperature; but increasing temperature produces more gases and carbon. Also platinum or palladium (0.5%) on zeolite base can abate the nitrogen attack. By using, platinum or palladium catalysts more isomeric structures can be produced than nickel or tungsten.

Molecular sieves⁵⁵ possessing large pores are currently used for hydrocracking operations. They exhibit high activity even in presence of hydrogen sulfide and ammonia due to large pores; further they are hydrothermally stable.

Sodium contamination⁵⁶ may deactivate the catalyst to a small extent but its presence is reflected in decreasing the octane number of gasoline.

Mordenite catalysts are also available but their activity and stability rapidly decrease. They are suitable for producing gases from naphthas.

Zeolite catalysts, loaded with noble or non noble metals form excellent catalysts, as they can operate in substantial concentrations of ammonia. Unicracking JHC processes operating on heavy feeds have successfully demonstrated the activity of these catalysts up to seven years⁵⁷.

As the cracking operations go on, to counter act the loss

of activity of catalyst, the reactor temperature is increased day by day by 0.5 to 1.0°C.

5.6.1.3 *Hydrocracking reaction conditions*

Usual temperatures of cracking fall in the range of 300—400°C, with high pressure of hydrogen between 60 to 150 atms. Relatively large amounts of hydrogen circulation is necessary to prevent fouling of catalyst which permits long runs of catalyst. To get high purity products, pretreatment of feed is essential. This pretreatment not only removes sulfur, nitrogen, arsenic etc. but ascertains products free from these impurities.

5.6.1.4 *Processes and description*

Most of the hydrocracking operations are carried out in fixed bed reactors only. Catalysts are very similar to cat. cracking catalysts. Present trend of using molecular sieves attired with rare earth metals in hydrocracking is in no way different from cat. cracking reactors. The process may be conducted in a single stage or in two stages. First stage reactor is bequeathed to give 40 to 50% conversion to gasoline while the heavy portion (from the effluent of the reactor) forms the feed stock for 2nd stage reactor where a 60% conversion is anticipated.

The catalyst in reactor is spread in a number of beds; this helps in locating the hot spots where cold hydrogen injection is planned. Hydrocracking processes of common interest are described below :

5.6.1.5 *Isomax Process*

This process employs a fixed bed catalyst system with a single stage operation. High selectivity and activity of catalyst brings all features in the design to handle stocks from naphtha to deasphalted residuums. Alternatively, Isomax offers a new route to hydrotreatment of lube oils. Important aspect of this process is low consumption of hydrogen; and with moderate temperatures of operation, a fresh charge of catalyst can maintain its activity from one to two years before any regeneration is attempted.

Charge stock, recycle hydrogen and make up hydrogen are mixed and passed through a heater. The mixture enters the reactor (1) from the top while cold hydrogen is admitted into the

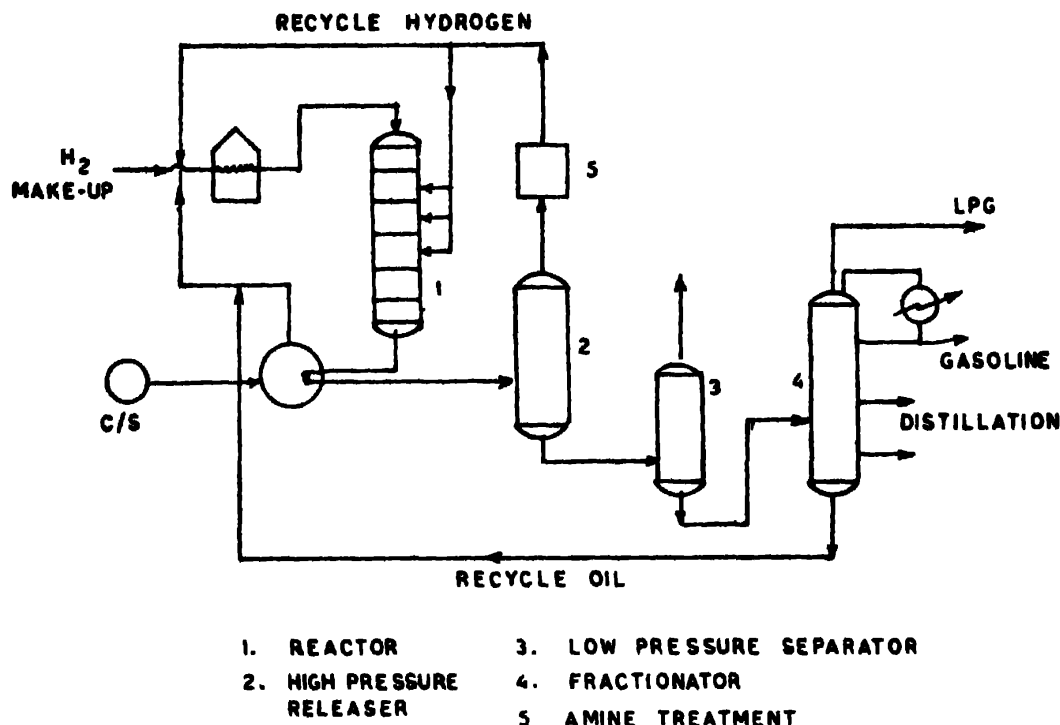


FIG 5 16. Hydrocracking (isomax)

reactor at different points (hot spots). The effluents from the reactor are immediately heat exchanged with the c/s, chilled and fed into a high pressure separator (2); where hydrogen is separated. This hydrogen is contaminated with H_2S and NH_3 ; hence a proper treatment for the removal of these constituents is required and is practised in the treater (5). The recovered hydrogen is compressed to the required pressure and recycled back. Treated stock from high pressure releaser goes to low pressure separator (3), where fuel gas (up to C_3 fractions) H_2S , are obtained. Liquid fractions from the bottom of this separator enter the fractionator (4), where distillates are separated. The heavy oil from the fractionator is recycled back to the reactor. Light gases, after congenial treatment can go into the fuel system.

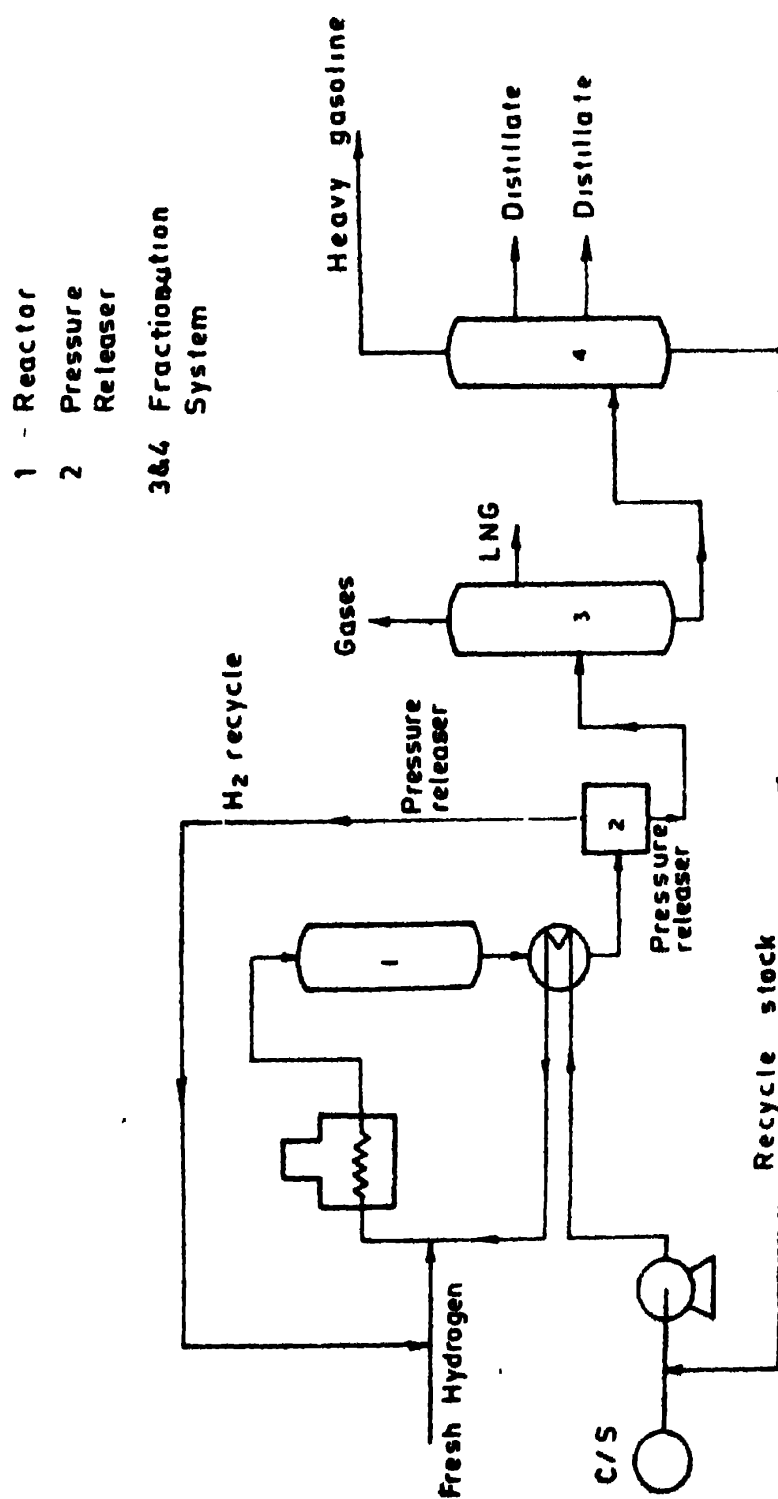


FIG. 5.17(a) Single Stage Hydrocracking System (HG.)

Operating conditions

Pressure of hydrogen	30 to 100 atmos.
Temp. of the reactor °C	250 to 370°C
Consumption of hydrogen	35 to 50 M ³ /per barrel

5.6.1.7 H. G. Hydrocracking

Gulf Research & Development Co. and Houdry Divn. had jointly developed this process. In this process, conversion of light and heavy gas oils into more valuable lower boiling products is accomplished. The process is designed for a single stage or two stage reactor system.

Fig. 5.17(a) shows single stage operation and

Fig. 5.17(b) shows two stage operation.

When two stage system is employed, mild hydrotreating operations take place in the first reactor; second stage sees through the hydrocracking reactions. Effluent from first stage reactor is cooled and hydrogen rich gas is separated for recycle as shown in Fig. 5.17(b). Effluent from the second stage is cooled and hydrogen is separated. Fuel gas and lighter fractions are separated. A distillation column fractionates the effluent into gasolines and distillate oils. The heavy portion of the oil may be recycled back into the second stage reactor.

Ultra cracking of Standard Oil Co. operates on similar lines as the above one. Catalyst is multi functional; these functions include denitrogenation, olefin and aromatic saturation and desulfurisation. Longevity of the catalyst has made the process more economical. A difference exists from the previous operations in introducing water directly into cold reactor effluent, which absorbs ammonia and partly hydrogen sulfide too. 100% conversion with a feed of 70/30 mixture of coker and heavy catalytic oils is most usual.

Unicracking—JHC developed by UOP and ESSO enjoys a good reputation in hydrocracking operations. All types of cycle oils and paraffinic raffinates can be successfully fed to the reactor system. More than 100% yield is achieved with low dry gas yield. Heavy gasoline from these units is good for reformers, thus the process has become important for production of aromatics.

All the fixed bed operations resemble one another. They differ only in the catalyst composition and feed stock and product pattern.

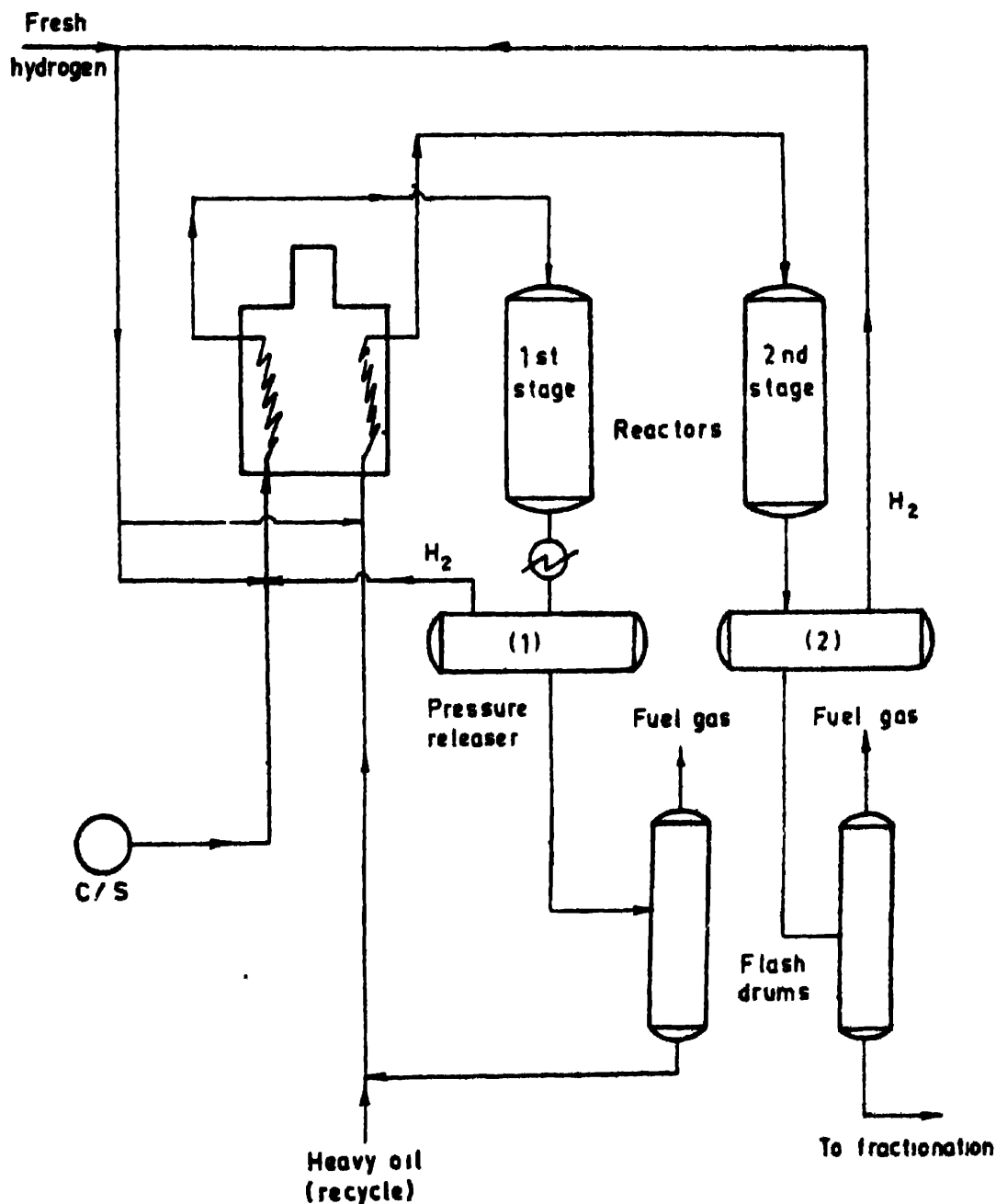


FIG 517(b) H G Hydrocracking (Two Stage)

5.6.2 MOVING BEDS (EBULIENT BED REACTORS)

Cities Service Research & Development Co. had developed this process. The high lights of the process is that it employs an ebulent bed instead of fixed bed ; which brings in extremely

efficient contact of catalyst, oil and hydrogen. Residues are converted to low sulfur fuel oils. Heavy gas oils and cat. cracker oils are hydrogenated. Its capacity to handle short residuums or stocks of high metallic content is striking. Since the catalyst bed is in ebullient condition, addition or withdrawal of catalyst during operation is no problem. A constant quality and rate of products can be remarkably maintained without much difficulty.

5.6.2.1 Moving Bed Hydrocracking Process (Fig. 5.18)

H—oil process is designed to process residuums or other heavy feed charges and usually employs a hydrogenating catalyst.

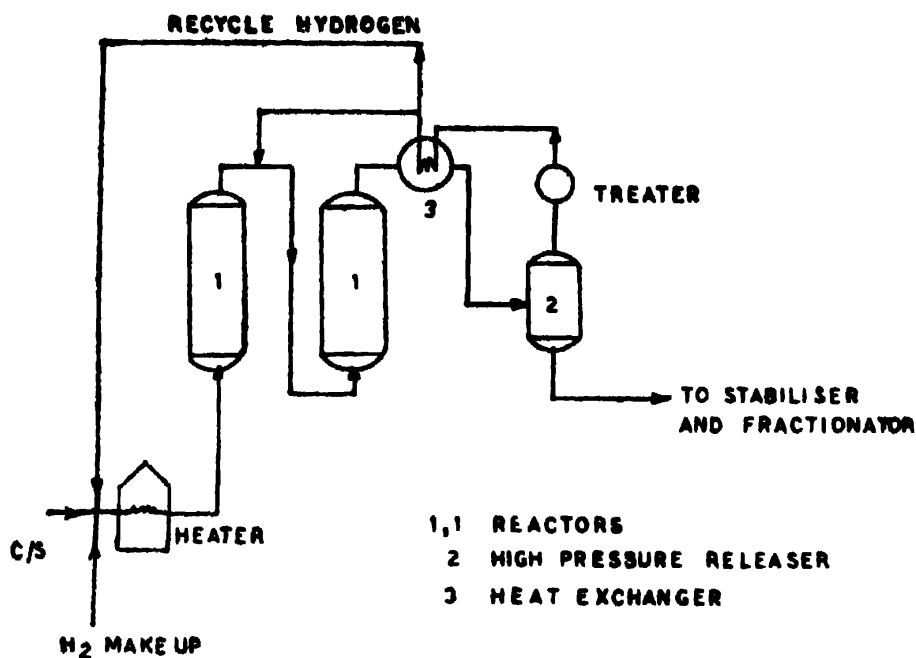


FIG 5.18 Moving Bed Hydrocracker

Hydrocracking process, was also developed by Cities Service Research and Development Company and Hydrocarbon Research. This process uses a dual function catalyst and can take up feeds upto a boiling point of 650°C. The major difference in these processes is that the catalyst is kept in moving condition. To achieve this moving bed conditions, charge is fed into the reactors from the bottom. The reactors two in numbers (1. 1) work serially. The effluents go from the top of the reactor. The

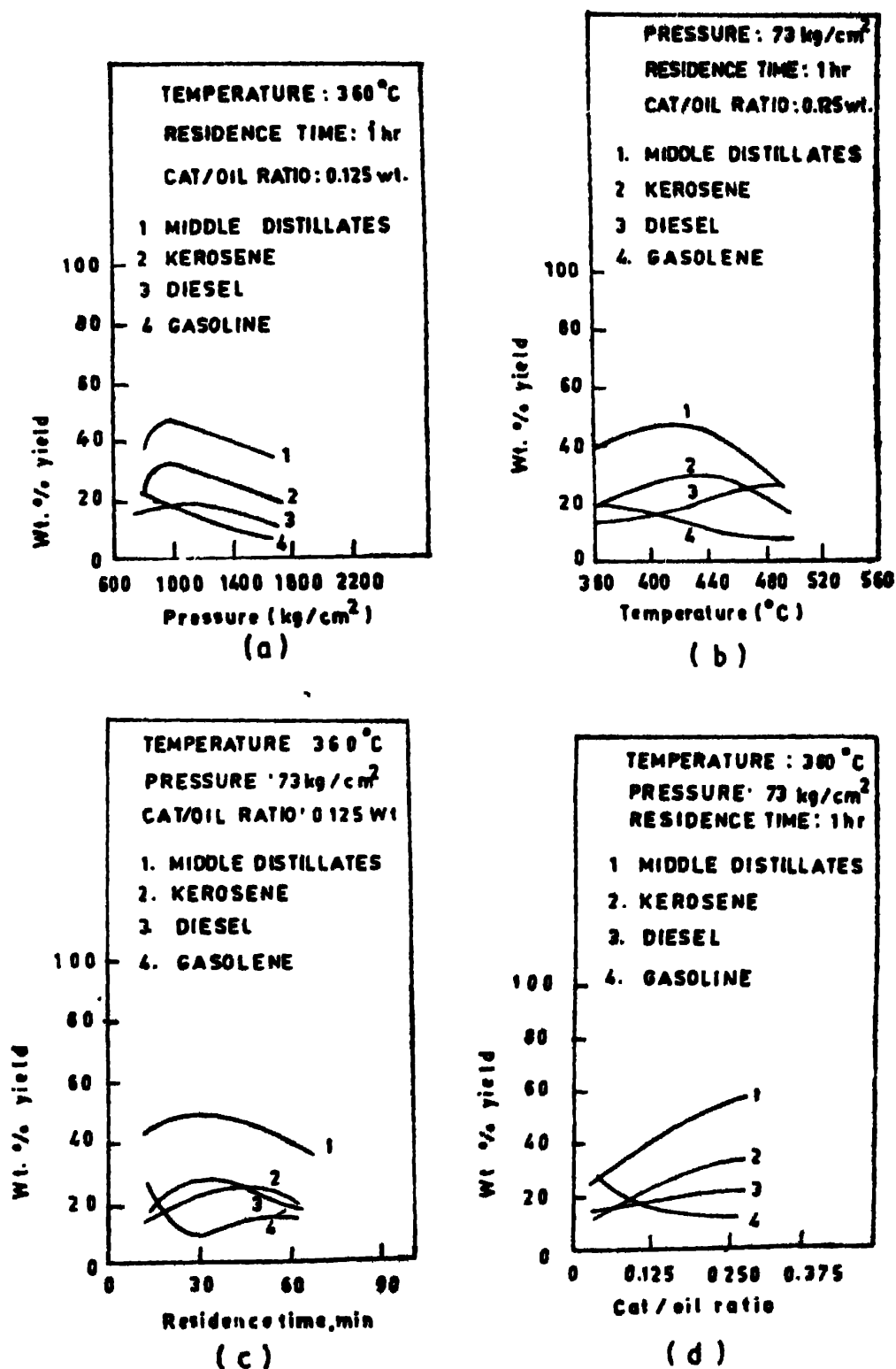


FIG. 5.19(a) Effect of Pressure on yields of distillates
 (b) Effect of Temperature on yields of distillates
 (c) Effect of Residence time on yields of distillates
 (d) Effect of Catalyst to oil Ratio on yields of distillates.

separation, recycling and fractionation follow the conventional procedure as is done in Isomax Process.

Operating conditions :

Pressure	200 atmos.
Temperature	400—460°C
Consumption of hydrogen	40 M ³ /bbl

Some of the laboratory results on hydrocracking of vacuum distillates for middle distillates are shown⁷⁰ in Fig. 5.19a, b, c and d.

5.6.3 HYDRODESULFURIZATION AND HYDROTREATMENT

Next to hydrocracking operation, hydrodesulfurization and treatment form major hydrogen processing operations. The difference between hydrodesulfurisation and hydrotreatment is marginal and work on the same technology including catalyst. Difference occurs mainly in operating conditions. Hydrotreatment in most of the cases may be treated as a finishing operation, while hydrodesulfurisation is mainly a technique of impurities elimination.

Though the name hydrodesulfurisation suggests the removal of sulfur, yet other impurities which can form hydrides are also simultaneously taken off.

The importance of hydrogen processes, either for desulfurisation technique or for treatment technique or production of lighter fractions by hydrocracking is ever enchanting and increasing. The refiners are thinking of introducing "All hydrogen"⁶⁸ refinery operations due to many advantages available by hydrogen processes.

5.6.3.1 *Hydrodesulfurisation* (HDS)

Hydrogen over a catalyst is capable of reacting with sulfur, nitrogen, halogens and oxygen, from the respective compounds available in the fractions. Sulfur, nitrogen and halogens escape as the respective hydrides, while oxygen escapes as water vapour. Metals found in the oil are generally adsorbed on the catalyst surface, hence the product shall always contain less

metals. However increase in metal concentration on the surface of catalyst naturally rescinds the activity of catalyst.

Increase of boiling point of feed also brings alarmingly increasing difficulties to the process. Thiophenic compounds are major sulfur compounds in the high boiling fractions, and these being lethargic towards hydrogen render desulfurisation more difficult. Mercaptans do offer such difficulties but to less extent, hence may be placed in intermediate region. Nitrogen is quite adamant and requires very severe conditions.

Bauxite with impregnation of molybdenum is capable of removing 70 to 80% of metals.⁵⁹ Demetallisation (Demex) processes are being tried extensively. In this method the removal of metal concentrates is done by solvent extraction resembling deasphalting operations by solvents. Manganese nodules⁶⁰ are found to be catalytically active in demetalation of topped crudes in presence of hydrogen. These nodules are cheaply available in marine and fresh water sediments. Manganese nodules deposited on CO—Mo on alumina base serve the best.⁶¹ Hung and Wei⁶² studied demetalation of porphyrins using CoO_3 -MoO₃ on alumina. The report shows that 90% of nickel and vanadium could be eliminated.

5.6.3.2 Catalysts

Two types of catalyst compositions are popularly used namely Nickel-molybdenum and Cobalt-molybdenum on alumina. Although both are active catalysts, still some reservations are observed with reference to Ni-Co compositions.⁶³ These compositions seem to be more active than Co-Mo catalysts, especially while removing nitrogen. Basically, the structure, particle size and porosity of the catalyst are irrefutable parameters in judging the activity and life of catalyst.⁶⁴ Sulfur in paraffins is easily removed, while the same in aromatics is quite resistant. Even Co-Mo catalysts at 350°C under a pressure of 100 atmos can remove 90% nitrogen.⁶⁵

Comprehensive studies on Ni-Mo (Shell 324) and Co-Mo (Shell 344) by T. F. Kellet et al. show⁶⁶ :

Ni-Mo catalysts are effective for removal of nitrogen ; hence these are suitable for treating cracked stocks.

H₂ consumption with these catalysts is more.

In general, increase in space velocity increases sulfur in products and hydrogen consumption.

As reaction temperature increases hydrogen consumption too increases.

With Ni-Co catalysts, pre sulfurisation with carbon disulfide or any sulfide is essential.⁶⁷ The fullest activity of these oxides occurs in fact after interaction with sulfur and a part of catalyst is converted into sulfides.

Widely used catalyst composition is given below :

Mo O ₃	12.9%—13%	by wt.
Co O	4.1%—5%	do
Na OH	0.6%	do
SiO ₂	1.0%	do
Sulfates	1.0%	do
Al ₂ O ₃	(by difference)	
Surface area	m ² /gm	200—320
Pore volume	c.c/gm	0.4—0.6
Bulk density	gm/cm ³	0.65 to 0.68
Shape	: Cylindrical of 1.5 mm dia×4	

Apparent activation energy : 7.83 to 12.58 K cals/gm

5.6.3.3 Process Variables

Partial pressure of hydrogen, temperature and space velocity are the principal operating variables for a chosen catalyst composition. Increase of partial pressure of hydrogen, suppresses the coke formation and enhances the reaction rate. High temperatures favour removal of nitrogen and thiophenic sulfur; but excess of temperature retards the reaction rate due to coke formation.

Reaction variables-conditions :

Hydrogen consumption	2.9 M ³ per barrel per 1% sulfur reduction ; 8 M ³ per barrel per 1% nitrogen reduction
Pressure	10—200 atmos.
Recycle hydrogen :	8 to 10 times consumption
Temperature	350—450°C

For olefin and aromatic hydrogenation extra quantity of hydrogen is required :

Yields for distillates	95 to 99%
for residues	85 to 90%

Sulfur reduction with	
naphthas and distillates	up to 95%
for fuel oils and residues	up to 50%

Fig. 5.20 shows the hydrosulfurisation operations. C/S and

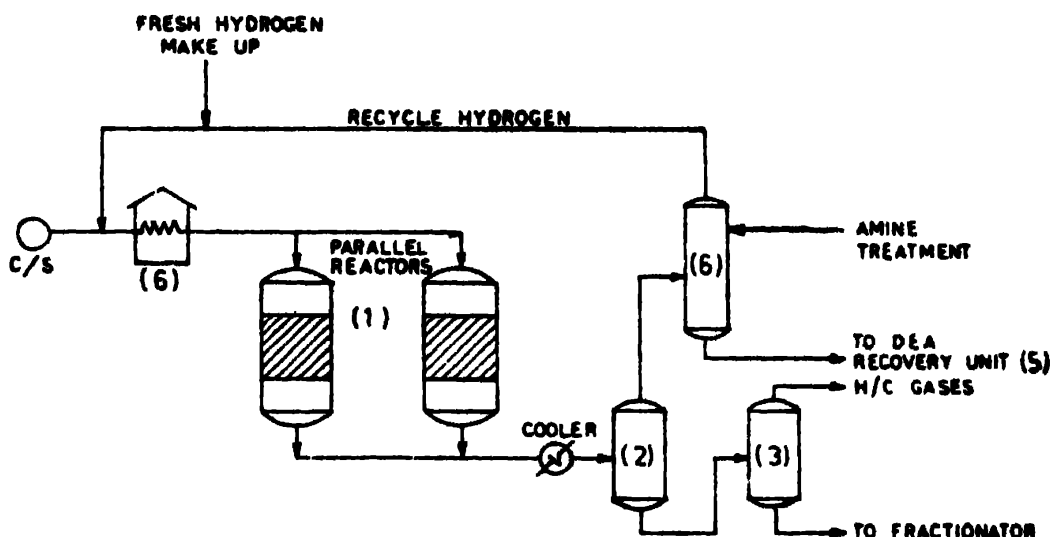


FIG. 5.20. Flow sheet of hydrosulfurisation Process

recycled hydrogen (fresh hydrogen) are heated in a furnace (6) and the vapor is fed into reactors (1) ; one or two stages may be employed. Some times reactors are arranged in parallel to increase the capacity of plant. The out going vapors are admitted into a high pressure separator (2) where H_2S , NH_3 etc. are freed along with unreacted hydrogen from the treated product. The product goes into a low pressure separator (3), where gases (hydrocarbon) are separated and the bottom product is transferred to a distillation column. Hydrogen from high pressure separator is associated with impurities formed in hydrotreatment. So the gas is purified by treating with amine solution(4). Pure hydrogen recycles back.

Catalyst composition

Co—Mo Metallic compounds on alumina pellets.

Temperature

350–450°C

Pressure	High, up to 100 atmos.
Space velocity	0.2 to 2 V/hr.V.
Sulfur reduction	90%
Ni+V ppm reduction	Up to 90% in light fractions Up to 60% in heavy fractions

Gulf HDS process is a fixed bed regenerative process. By varying the reaction conditions light distillates can be processed. Regeneration is carried in situ by blowing air steam at 400 to 500°C. A safe period of 4 to 5 months at desulfurization levels of 65 to 75% is quite attractive, before any regeneration is attempted. Low cost catalysts with high activity are proprietary of Union Oil Comp. These catalysts enable the operation at reduced pressures (40--60 atmos) for feed stocks of diverse nature. Gulf (HDS) process on Kuwait residual oils shows a removal of sulfur from 3.8% to 0.1%, with improved quality of gasoline; yet requiring 33% less reactor volume.

HDS product inspection⁶⁸

	Reduced crude	—	Desulfurised gas oils
A P I	249		344
Sulfur % (38)	0.11		0.07
SUS 988	61		1.49 cs
386	456		40
P. pt. °C	—1		—1
Carbon residuc	2.32		0.09
N ₂ wt. %	0.08		0.08
Vanadium } (60) ppm	0.3		0.1
Ni	0.3		0.1 (Figures in brackets show the amounts in raw material)

5.6.4 HYDROTREATMENT/HYDROFINING

These operations are treated as finishing operations. Different fractions require characteristic finished properties, hence the operation is selective to each fraction. Colour, stability and odour are the selective parameters and improvement in these makes the product more valuable.

For naphthas and gasolines :

Treatment improves colour, odour and stability. Removal of sulfur is essential before feeding to reformers. Susceptibility to lead is increased if the sulfur is removed.

For Kerosene and Jet Fuels

Besides improvement in colour, odour and stability; smoke point improvement is added advantage. Conversion of aromatics to naphthenes results in quantity and quality of these fuels. Diesels also fall into this category. Though much saturation is not anticipated, still removal of pollutants is highly commended.

FOR LUBES

Viscosity index improvement is a great achievement.⁶⁰ This treatment thus saves the valuable material in going as loss. Eliminates to certain extent refining and acid treatment.

Some of the trade names of the processes instituted for different purposes :

5.6.4.1 *Autofining/Objectives*

Desulfurization of distillate stocks. Preparation of feed stocks for steam reformers and SNG plants.

Arofining/Objectives

Reduction of aromatics helps in producing quality jet fuels. Aromatics free solvents and less aromatic feed stocks for some cracking operations.

Gulfining

Production of low sulfur fuel oils or cat. cracking stocks.

HPN

Selective hydrogenation and desulfurisation Hydrogenation of C_3-C_4 olefins and diolefins.

Hydrogenation of cracker naphthas.

Hydrobon

Objectionable materials are removed from petroleum distillates. Sulfur in naphtha may be reduced to 0.5 ppm.

5.6.4.2 *Hydrofining*

Removal of sulfur from wide range of distillate feed stocks. Improvement in colour, stability and odour.

Lube hydrofinishing

Improves colour and stability of lubricating oils. Reduction in impurities and improvement in viscosity index.

Ferrofining

Solvent refined lubes are treated. This eliminates acid-clay treatment of lube stocks, employs rugged three component catalyst.

Ultrafining

Desulfurization, denitrogenation and saturation of olefins. Naphthas, Kerosenes and diesels decanted oils are treated. Employs CO, Ni & Mo catalysts. Low pressure and low temperatures with minimum consumption of hydrogen.

Unionfining

Desulfurization and denitrogenation of wide variety of petroleum stocks. Mainly used for cat. cracking feed stocks and kerosene desulfurization.

5.6.4.3 Hydrofining operation

This process is versatile in industry, with proper choice of catalyst and conditions, impurities are removed and burning characteristics of virgin and cracked materials are improved. Naphtha to reformers (steam/catalytic) must have as low as 5 ppm of sulfur and nitrogen ; otherwise the bimetallic catalysts

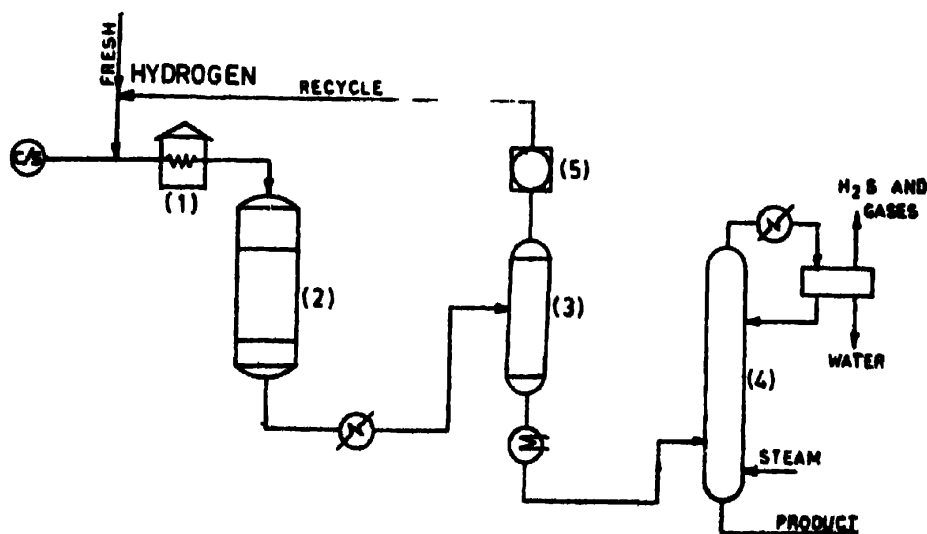


FIG. 5.21. Hydrofining operation

are easily poisoned. It may be treated as a sweetening technique for such feeds. High quality diesels and kerosene can be made from even sour crudes.

Fig. 5.21 shows the outline of the process.

Feed stock and hydrogen (recycle + make up) are mixed and heated in a furnace (1). The mixture is passed through reactor (2) containing Co-Mo oxide catalyst. Reactor conditions range from 250 to 450°C and 10 to 80 atmos. depending upon the degree of treatment and boiling point of feed. The reactor effluents are heat exchanged and purged in a pressure releasing drum (3). Recycle hydrogen after treatment with different solutions (5) to absorb H_2S and NH_3 , compressed and mingled with the make up hydrogen. The products are stripped (4) to remove light gases and remaining hydrogen sulfide; the bottoms of the stripper constitute the treated product. Catalyst is not generally regenerated but replaced after 12 to 14 months.

5.7 Alkylation

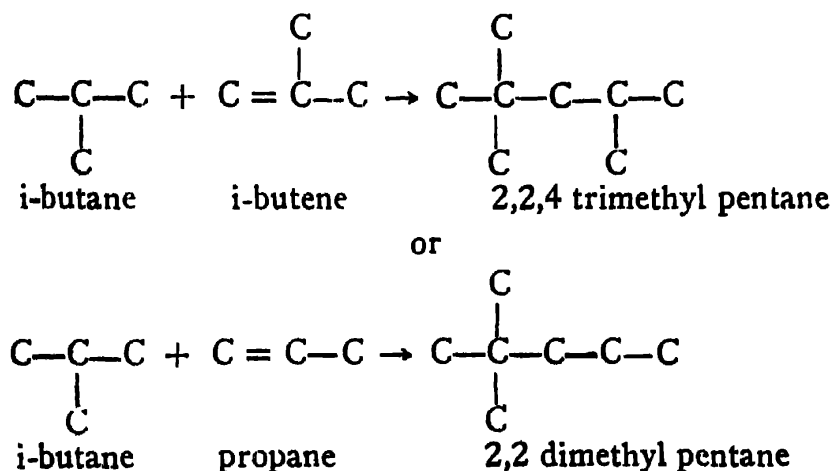
At present alkylation processes are gaining importance; high quality blends of motor fuels can be obtained by this method.

Alkylation processes are conducted on a large scale. Equivalent to 2% world crude refining is earmarked for this operation alone signifies this statement.⁷¹

Alkylation processes are conducted by Lewis acids like sulfuric, hydrofluoric acids and aluminium chloride. 60% of alkylation is done by sulfuric acid, while the rest is done by hydrofluoric acid; this shows sulfuric acid has got certain advantages over HF. Aluminium chloride is not used very much for alkylation purposes. Sulfuric acid process requires a very low temperature, usually less than 15°C to prevent oxidation of the products; HF can operate fairly well upto a temperature of 35°C. During alkylation, sulfuric acid undergoes marked changes. Fresh acids give low yields of alkylation, while circulating acids give improved yields.⁷² Some additives are also added to decrease the consumption of acid and increase the yield of alkylate.⁷³ Alkylation reactions are exothermic hence heat removal is essential. This is done by evaporating propane in the reactor.

Feed Stock and reactions

Alkylation is reverse of cracking, it joins an olefin with a paraffin. In fact an i-paraffin is chosen, so that production of a tertiary carbonium ion is favoured. Useful raw gases for this reaction are propene and i-butane. In spite of components higher than butane can be alkylated, it is not desirable here, due to the fact that there will be a great increase in boiling point. For example, i-propane as such is having good octane number, it gives low vapour pressure to gasolines when blended. Further, with propane, and amylene, the alkylate produced is stable in presence of acid whereas i-pentane⁷⁴ produces higher alkylates having relatively less stability. A high ratio of i-paraffin to olefin (not less than 5) is maintained in the reactor. A contact time ranging from 30 to 60 minutes is usually sufficient. Unconsumed i-paraffin is always recycled back to increase its concentration in the reactor. Reactions proceed via carbonium ion mechanism as shown below :



In sulfuric acid alkylation, acid of 93 to 95% strength is used (higher strengths of acid can cause the reactions at lower temperatures). Sulfuric acid alkylation is done by two well known processes, namely Cascade and Effluent Refrigeration. The differences between the two processes are in reactor design and how propane and butane evaporate in the system to induce refrigeration.

5.7.1 CASCADE SULFURIC ACID ALKYLATION

In this a multistage cascade reactor system (fitted in each

stage with a mixer) is employed. Hydrocarbon and acid pass from one stage to other cascading serially; Olefin is split and introduced into each cascade. The formed alkylate is taken out from the top of cascade reactor, cooled and fractionated. i-Butane from the fractionator is mixed with the incoming feed and sent into reactor. Acid from the bottom of the reactors is taken and kept in circulation, necessary fresh addition of acid is also continued. Propane evaporation causes self refrigeration and maintains the temperature of alkylation at required low level. Propane leaving reactor with butane stream, is compressed cooled and fractionated to recover back the refrigerant for circulation. Fig. 5.22 shows the process flow sheet.

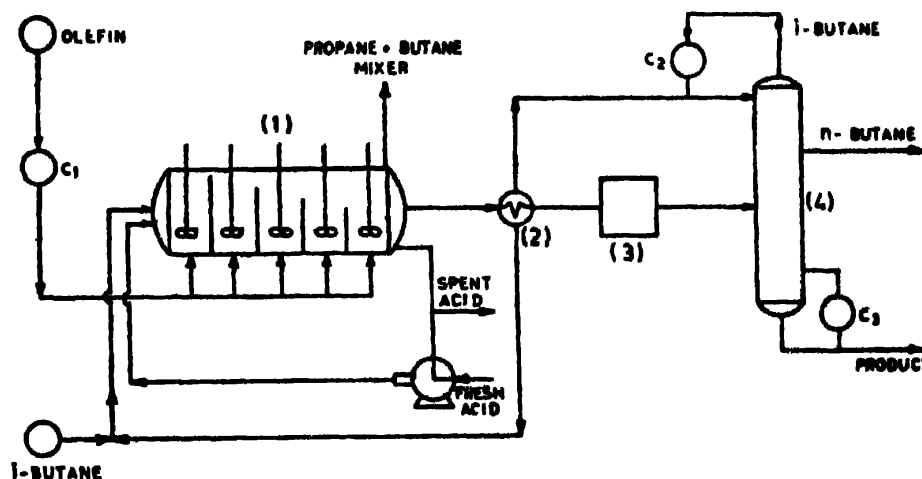


FIG 5.22. Sulfuric Acid Alkylation

- (1) Cascade Reactor (2) Heat Exchanger
 (3) Caustic wash section (4) Fractionator
 C₁ & C₂ Coolers
 C₃ reboiler

5.7.2 H. F. ALKYLATION

There are two commercial processes employing HF as catalyst. These are licenced by Phillips Petroleum and UOP Companies.

The essential features of the process are shown in Fig. 5.23. Olefin and i-butane feed (1 : 5) is dried and mixed with recycling acid. The mixture is passed into reactor; the reactor acts as settler also. After reaction is completed mixture is allowed to

settle into two liquid layers. Acid layer is removed from the bottom of the settler, cooled and recycled. Fresh acid is supplemented whenever required. A part of acid is stripped to remove

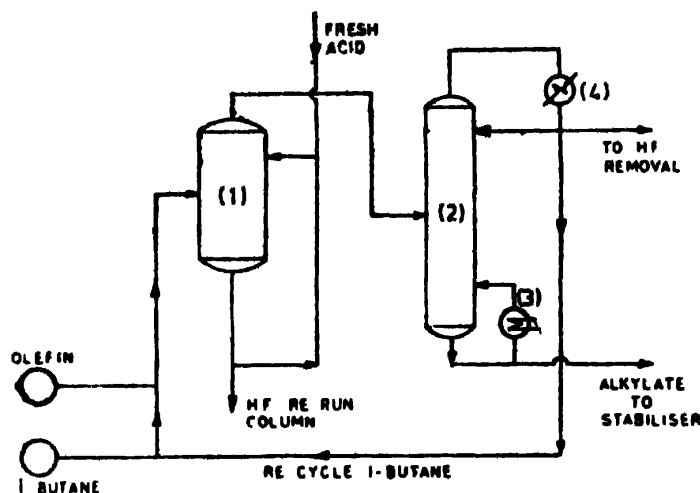


FIG. 523 Hydrafluoric Acid Alkylation

- (1) Reactor (2) Fractionator
(3) Reboiler (4) Cooler

water and polymer products. Acid, free from these, is again mixed with the circulating acid.

Hydrocarbon layer removed from the top of the acid settler contains unreacted constituents and alkylate along with small amounts of acid. The components are separated by fractionation and i-butane is circulated into the reactor. The flow sheet does not show complete rectification system. Alkylate from the bottom is again stabilized to separate i-butane. i-Butane leaving from these columns is fed back to the reactor. Acid re-run plant is also not shown in the flow sheet.

A minimum pressure in both the alkylation systems is essential to increase the partial pressure of reactants and decrease the volatility. The properties of both these acids is shown below. It is explicit, that HF is soluble in hydrocarbon layer up to 0.5%. That is the reason, why a separate distillation plant is required to recover the HF from alkylates; while this trouble may not be there with sulfuric acid.

Properties of acids :

	Sulfuric acid	Hydrofluoric acid
B. P. °C	290	19.4
Freezing point °C	+3	-83
Sp. gravity	1.84	0.99
Viscosity (CP)	3.3 (15°C)	0.26 (0°C)
i. C ₄ H ₁₀ ; in 100% acid	—	2.7 at 27°C
Solubility		
-do- in 99.5% acid	0.1 (13°C)	—
Solubility of acid in hydrocarbon layer :	} —	0.5%

AlCl₃ alkylation proceeds in presence of HCl gas,⁷⁵ (8 to 15 moles per 100 moles of feed gas). The catalyst can be in complex form with hydrocarbon diluents or can be used in dry state. About 170 gallons of alkylate is obtained per kg. of salt.

5.8 Isomerisation Processes

Conversion of normal paraffins into isoparaffins helps in two ways. Good quality gasoline due to improvement in octane number is the essential result of an isomerisation process. For alkylation purposes, isoparaffins are required because the straight run products naturally can not meet such demands ; hence isomerisation of straight chain compounds is inevitable.

Feed stocks suitable for such operations should mainly consist of C₄, C₅ and C₆ fractions. Isomerisation may take place in vapour phase or in liquid phase with a dissolved catalyst.

Process Description :

All types of catalysts used in cat. cracking and reforming operations are certain to bring about this reorientation of molecules⁷⁶. At present aluminium chloride catalyst is vastly employed. This catalyst can be used in fixed beds or in liquid contactors. Noble metal catalysts are generally employed in fixed beds only.

5.8.1 ISOMERISATIONS WITH PLATINUM CATALYST

The catalyst used in this process is similar to platinum base catalyst used in catalytic reforming operations. The main difference is in number of reactors and reaction conditions. Unlike platforming operations, there is only one reactor in this

Conditions of reactor :

Space velocity $\left(\frac{V}{hr. V}\right)$ 2 to 3

5.8.1.1 Aluminium Chloride process

The diagram illustrates a fluid catalytic cracking (FCC) process. Feed stock enters a reactor (1) where it is contacted with catalyst. The reactor effluent goes to a separator (2) where sludge is removed. The catalyst is then recycled through a series of vessels (3, 4, 5) and a final separator (6) before returning to the reactor. Recycles for HCl and Hydrogen are shown at the top. Fresh catalyst is added to the reactor. The final product is n-Paraffin.

- | | |
|------------------------------|------------------------|
| 1. REACTOR. | 4. HCL STRIPPER. |
| 2. CATALYST RECOVERY SYSTEM. | 5. CAUSTIC NEUTRALISER |
| 3. HYDROGEN STRIPPER. | 6. FRACTIONATOR. |

Isomerisation process.

FIG. 5 24. Alluminium Chloride Isomerisation Process

in isomerisation process using fixed bed aluminium chloride catalyst. Desulfurised and moisture free feed stock (C_3/C_4) with recycled *n*-paraffin is mixed with hydrogen and heated (not shown in figure). This mixture with recycled HCl gas enters the reactor (1); where the catalyst is spread on alumina or bauxite in a fixed bed.

The effluents are passed through a catalyst recovery system (2) and then through a pressure releaser (3) where hydrogen separates out. Later HCl gas is recovered in a stripper (4). The effluent is given a caustic wash (5) and finally sent into a fractionator (6) to separate *i*-paraffin at the top and *n*-paraffin at the bottom. *n*-paraffin is recycled back.

Reaction conditions :

Temperature °C : 180 to 250
Pressure : 20 to 50 atmos

Space velocity $\left(\frac{V}{V-hr}\right)$: 10

Hydrogen requirements : 2 to 6 M³ per bbl.

HCl wt% : 4 to 5

Aluminium chloride, when used in liquid contractors is generally dissolved or made into a slurry in hydrocarbon liquids. The tendency for aluminium chloride to form complex with these solvents increases, hence a feed stock higher than butane is likely to carry more aluminium chloride fig. 5.25 shows the operation in liquid phase.

Paraffin feed (1) is first dried in a dryer (2) and heated to 60 to 100°C in a heat exchanger (3). The feed now passes into a catalyst scrubber (4), where it can remove the catalyst entrapped in heavy sludge obtained in the process. The feed is then mixed with hydrogen, and hydrogen chloride vapours and allowed to enter the agitator reactor (5), where fresh/recycle catalyst is always present.

The effluents are then washed with water/alcohol to remove the catalyst in a wash column (6). The light hydrocarbon layer is led into an accumulator where hydrogen and hydrogen-chloride are separated. Heavy, settled hydrocarbon layer is circulated back to wash column while some product is taken to

a stripper where remaining HCl vapours are driven off. Light paraffins recycled back, while i-paraffin is obtained at the bottom.

The conversions are likely to exceed 60% with all types of feeds.

Some processes of industrial significance are given below :
Hysomer Process : (Union Carbide/Royal Dutch/Shell)

It is aimed to improve the octane number of gasolines containing rich amounts of pentanes and hexanes. Hydro cracked stocks are generally rich with such components. In this process noble metal deposited on zeolites, capable of offering dual functions, is employed as catalyst. These catalysts are capable of taking feeds containing sulfur and water upto 35 and 50 ppm respectively. Hydrogen consumption is very low, 0.1 to 0.3% by wt. The catalyst is regenerable.

Operating conditions :

Temperature	250 to 300°C
Pressure	15 to 30 atmos.

$$\text{Space velocity} \frac{V}{\text{hr.} \cdot V} \quad 1 \text{ to } 3$$

Octane number improvement is generally 6 to 10 units.

5.8.1.2 *Pcnex (UOP)*

Pentanes or hexanes are isomerised over platinum containing catalysts.

Operating conditions :

Temperature	--	125 to 180°C
Pressure	—	20 to 70 atmos
Octane improvment	—	6 to 10 units
Conversion	—	upto 100%

5.8.1.3 *Isomate Process*

Aluminium chloride complex as catalyst with anhydrous hydrogenchloride promoter offers non regenerative isomerisation process.

Operating conditions :

Temperature	110 to 125°C
Pressure	up to 30 atmos.

5.9 Polymer Gasolines

Polymer gasolines actually represent dimers and trimers of olefins. High molecular weight polymers form a separate chapter.

Polymerisation is intended to convert off gases of thermal crackers. This can be accomplished in thermal units or catalytic units. In fact purification of the stream is not essential as the catalysts are capable of converting olefins even in presence of other diluents. Thermal polymerisation is not very effective, hence only catalytic polymerisation is industrially opted.

Olefin polymerisation is brought about by certain catalysts,⁷⁷ like copper pyrophosphates on charcol, sulfuric acid, phosphoric acid; at low temperatures not exceeding 200°C, and at pressure of 10 to 80 atmospheres. The reaction is exothermic liberating 225 to 300 kcals/kg. of polymer formed.

Process Description

The feed stock consists of C₃ & C₄ olefins (40 to 60%) obtained from crackers.

Catalyst is phosphoric acid deposited on carriers of inert nature (Quartz, Kiesulguhr etc.). The reaction is exothermic and is controlled by admitting cold feed stock into the reactor. If Tubular reactors are used they can be controlled by water or oil circulation. The process is shown in Fig. 5.26 and is almost

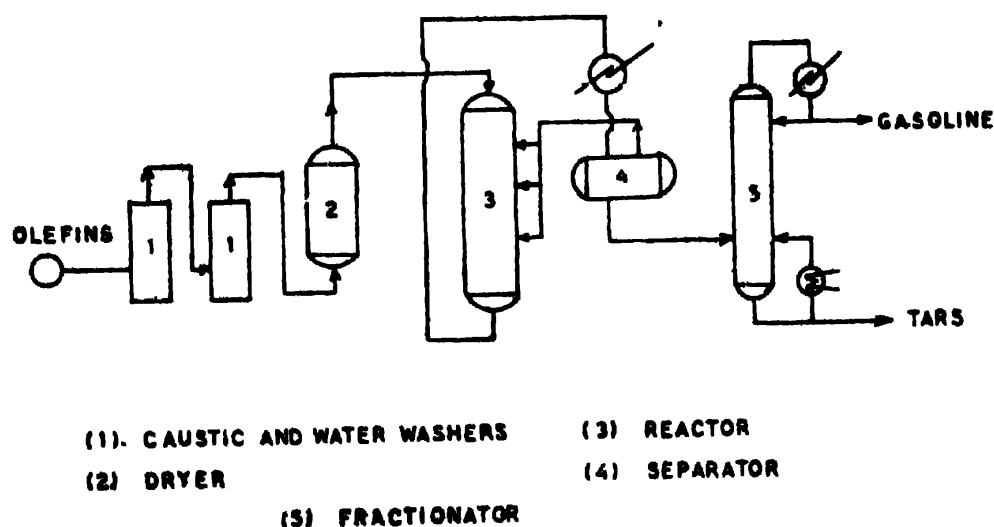


FIG. 5.26. Flow diagram for Polymer gasoline

similar to alkylation process. The off gases from the crackers are first washed with caustic and water (1). The gases are then passed through a dryer (2), enter the reactor (3). The effluent from the reactor enters through a cooler into pressure releaser (4) where condensed gasoline is collected and recycled gas is separated. The liquid fractions are now taken into fractionator (5) where polymer gasoline is obtained from the bottom of the column. Unreacted gas escapes from the top of the tower.

The reactions can be conducted at low pressure or high pressure. The life of the catalyst is less when low pressure is used,⁷⁸ about 70 gallons of polymer can be produced by a kg. of catalyst; high pressure reactors can yield 140 gallons of polymer per kg. catalyst. The polymer can give an octane number of 94 to 97

Sulfuric acid of 65% strength at an operating temperature of 30°C is sufficient.⁷⁹

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Exercise

- Relative velocity of a cracking reaction of a heavy oil at 490°C was found to be 18.8. To operate at 70 kg/cm² pressure the coil volume was increased by 10% per barrel. The temperature correction at this pressure was 0.38. Calculate soaking factor. Find the additional volume of the coil for cracking 100 lbs. of oil per hour.
(Ans. S.F. 0.071, Vol. 24 liters)
- Explain briefly the effect of steam in a naphtha cracker.
(b) Full range naphtha (45-180°C) is cracked at a rate of 5 tons/hr. Assuming different steam to hydrocarbon ratios estimate the optimum ratio of steam to hydrocarbon for producing maximum olefins.
- How do the different homologous series influence cracking pattern. If the feed stock meant for thermal cracker is wrongly delivered to a hydrocracker, what sort of repercussions may be anticipated.
- A delayed coker is designed to process 1000 kg/hr of a feed stock consisting of atmospheric bottoms and lube extracts. The average C C R was found to be 31.3%. Calculate the following.
(a) The amount of coke and gas produced per day.
(b) The C C R of products is 10, find C D E.
- Calculate heat of combustion of a mole of methane from the available data.

Heat of formation at 0°C	kJ/kg mole
Methane	— 72,000
Water (l)	—272,500
Carbon dioxide (g)	—376,220

(Ans. 212 K cal/gm mole)

6. Find the heat of decomposition per kg. gasoline produced in vis breaker which handles 7000 bbs/day of a charge of properties given below :

Feed stock	$C_{20}-C_{10}$
ρ at 30°C	0.825
Heat of combustion	36 $\text{M}^2\text{J/kg}$

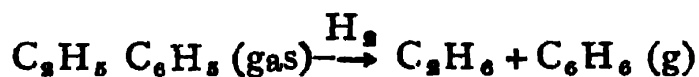
Products	Yield %	Heat of Combustion $\text{M}^2\text{J/kg}$	Mol. wt.
1. Gas	2.2	38.5	32
2. Gasoline	12	44.5	80
3. Middle fraction	28	41.3	190
4. Full oil	29	38.2	295
5. Residue	25	30.5	480
6. Rest, losses.			

(Ans. 3.14 $\text{M}^2\text{J/Kg}$)

7. From the data (Prob. 6) find the activation energy per Kg. gasoline produced
Time of cracking is 20 minutes at 400°C .
($C=30$)

(Ans. 52,303 K cal)

8. The following reaction was studied in a hydrocracker. The equilibrium constant at 25°C and one atmospheric pressure was found to be 0.03; find the equilibrium const. at 400°C , pressure remaining same.



$$\Delta H = -2600 \text{ K cal/Kg mole.}$$

(Ans. 2.49×10^{-3})

CHAPTER 6

Asphalt Technology

6.1 Source of Asphalt (Bitumen)

Asphalt is obtained as the ultimate bottom product of a vacuum distillation column. The residuums may still contain some oil, but further distillation serves no use at all. These residuums are rich in asphalts and form the starting materials for air blown bitumen. Asphalts are also obtained in large scale, from deasphalting units. Reduced crudes, waxy distillates, lube oils and long residuums are usually deasphalted for getting quality lube oil base stocks. Naphthenic crudes leave more asphaltic bodies in high boiling fractions, hence deasphalting operations are necessary for producing bright stocks and quality lube oils.

Cat. cracker feed stocks are also necessarily subjected to deasphalting operations.

6.1.1 CHEMICAL STRUCTURE OF ASPHALT

Asphalts do not have general representative formula and are very complex in nature exhibiting inconsistent properties. Asphalts are colloidal in nature and contain asphaltenes in oil which are stabilised by resins to maintain the colloidal form. A sample of asphalt contains :

Oil	—	35 to 50%
Resins	—	5 to 20%
Asphaltenes	—	20 to 30%
Acids etc.	—	upto 10%

Asphalts obtained from vacuum distillation units shall

have less pour point (usually between 30 to 60°C) where as asphalts from deasphalting operations show a high pour point (45 to 90°C). Asphaltic materials are usually responsible for some of the physical properties of crude oils. High sulfurous crudes give more asphaltic materials.

Asphaltic materials are black in colour and display agglutinating properties and hydrophobic tendencies. These are the properties which are industrially explored for road making and water proof works.

Structure of asphaltic materials has been the subject for numerous investigations. These investigations have revealed the significant details of the structure.

Most of the asphaltenes contain carbon to an extent of $82 \pm 3\%$ and hydrogen to $8.1 \pm 0.7\%$. It can be seen that the carbon hydrogen ratio is greater than 9 but surprisingly the ratio for various asphalts remains same. Nitrogen, oxygen and sulfur are the usual hetero elements present in asphalts in varying amounts. With increasing aromaticity and hetero elements, the molecular weight of the material also increases. Oxygen content vary from 0.3 to 4.9 and sulfur content reach upto 10%, while variation in nitrogen content is not appreciable—goes upto 3% only.

The structure of asphalts has been open to question for some time.¹ The present NMR studies show that they are condensed aromatic structures of sixteen carbon atoms or more. The idea of such big molecule may be difficult to conceive. X-ray analysis has furnished the valuable information regarding the dimensions of interlamellar distance, layer diameter and height of unit cell.

Indeed, the solubility of asphalt in different solvents varies. This advantage has been capitalised in precipitating different grades of asphalts by the use of solvents.

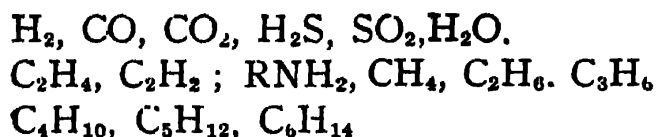
Sulfuric acid² is quite destructive to asphaltenes. Some salts like aluminium chloride can successfully remove the last traces of asphaltenes. The facile interactions of metal chlorides with asphaltenes may prove as a possible means of petroleum deasphalting in future.

The molecular weight of asphalts vary considerably from 900 to 2000 or even more, but no structural investigations have

emphasised the nature and location of the inorganic materials in these asphalts.

6.1.2 ACTION OF HEAT ON ASPHALT

Thermal cracking of asphalts result in more or less the same products as contemplated in heavy oil cracking. Thermal decomposition of asphaltenes is a good method for identifying and estimating the hetero atoms. A spectrum of compounds like saturates, unsaturates, and oxidation products are obtained during thermal decomposition of asphalts. Some of the decomposition products of asphalt are :



Dealkylation of aromatic rings at low temperatures ; and formation of benzene and naphthalene structures at high temperatures are quite contrary but pronounced.

However, the oxidation of asphaltenes by common oxidising agents like acetic acid, peroxides etc. is exceedingly slow. Phenolic and carboxyl groups are formed during oxidation. There is some up-take of oxygen by the molecule which effectively results in decreasing the solubility of asphalt in heptane. During oxidation dehydrogenation also takes place, with the result, unsaturates and aromatics tend to increase. Blowing air through asphalts brings about orientation in molecular structure, usually decreasing the molecular weight but producing necessary functional groups to give more agglutinating properties. Moschopedis³ et al have shown that during oxidation of asphaltenes oxygen to carbon ratio increases with increase of time, further the colour and consistency are progressively increased.

6.1.3 TYPES OF ASPHALTS

Asphalt is categorised into three distinct species, depending upon the source. The primary source is the residuums of vacuum distillation unit, second source is from deasphalting operations. Third is a mixed source comprising all the above two and solvent extracts. The necessary qualities like ductility, penetration index and API gravity are not available

with these raw stocks ; hence are to be imbeded. Some qualities are enhanced by air blowing of asphalt, the product of which is commercially known as air blown bitumen

6.2 Air Blowing of Bitumen

Air blowing is done mostly in batch units although continuous air blowing of bitumen is also in existence. In this operation, asphalts from various sources are mixed and heated to a temperature of 200 to 210°C and sent into the reactor. Fig. 6.1

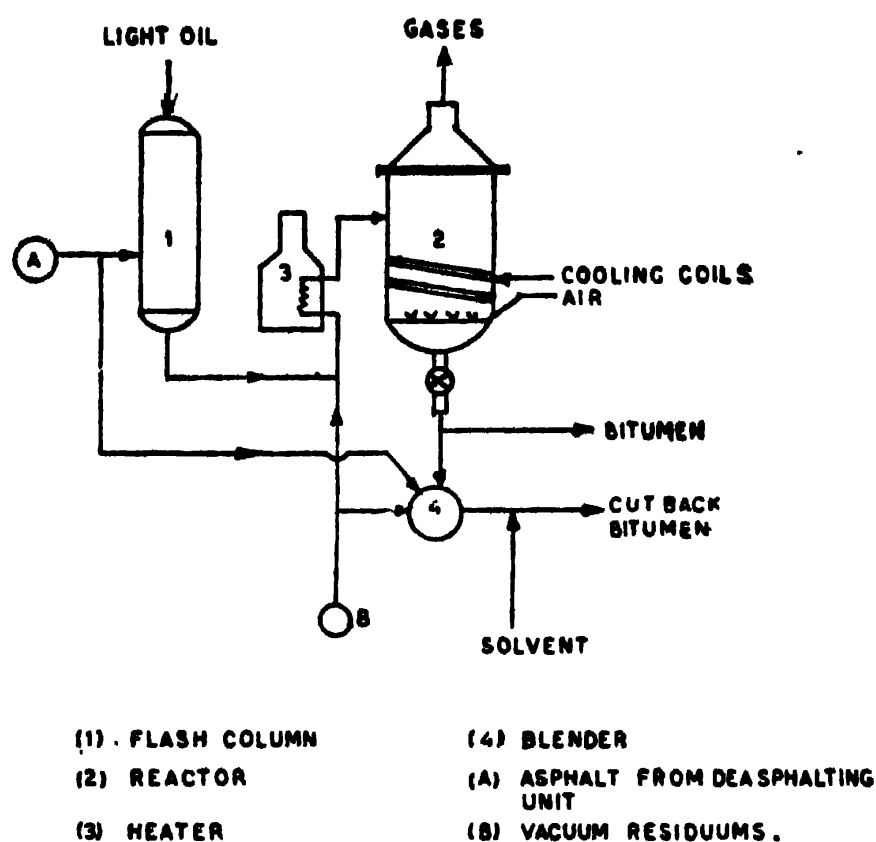


FIG. 6.1. Bitumen Blowing

shows the outlines of the operation. The reactor may be horizontal or vertical type, usually made of mild steel, of a capacity to hold 1000 tons of charge stock. These reactors are fitted with air distributors at the bottom and also cooling and heating coils. During oxidation the temperature may increase rapidly, hence as a precautionary measure provision for cooling is made available.

The reactor should be maintained at a temperature of 200 to 320°C, and air rate of 0.5 to 1.5 m³ at a pressure of 1.1 to 1.2 Kgs/cm² per hour, per ton of charge stock is necessary.

Blowing time lasts for 10 to 14 hours depending upon the required consistency of bitumen. Heat of reaction⁴ is dependent upon the consistency of bitumen as shown below :

Initial softening point °C	Final softening point °C	Heat of reaction kJ/Kg.
41.4	120	16.9
21.7		170.75

Gases are allowed to escape into refinery flare up or/ combustion system after being stripped with water.

The product, air-blown bitumen is obtained from the bottom of the reactor.

With sulfur also oxidation is possible and the product is found to have the comparable qualities as with air blown bitumen ; but the cost of such process is exorbitant.

The time of air blowing can be considerably reduced by adding certain chemicals like ferric chloride⁵, phosphorous pentoxide etc. A concentration of 0.3% ferric chloride is found to reduce the air blowing period by half.

Cut back bitumens are not really manufactured ones, but blended ones. These are obtained by blending various asphalts with a suitable solvent ; in fact these are liquid bitumens. Their action prevails after the solvent is dried off. These are mostly cheap grade bitumens. Simple blending of asphalts also may serve common needs.

Penetration index, the most important property of bitumen judges the quality of bitumen. Arbitrary estimation of penetration index is possible⁶ if the softening point (Ball and Ring method) is known ; by the following correlation :

$$\frac{20 - \text{P.I.}}{10 + \text{P.I.}} \times \frac{1}{50} = \frac{\log 800 - \log \text{P.I. at } T^{\circ}\text{C}}{\text{Softening point at } T^{\circ}\text{C}}$$

This equation is based upon the assumption⁷, that penetration index of all asphalts at softening point is approximately 800.

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ERRATA

Page No.	To be read as
24 Isoprene	$(\text{CH}_3) = \text{CH}_2$
Piperylene	$= \text{CH}.\text{CH} =$
25 cyclopentyl.cyclohexyl	first ring cyclopentane
52 K	$\frac{\sqrt[3]{R}}{0.823 \rho}$
53 Correlation Index	$\frac{48640}{T_B} + .$
74 Wobbe No.	$\frac{\text{Heat of combustion}}{(\text{Sp. gravity})^{0.5}}$
113 Flash point	0 54 $^{\circ}\text{C} - 69.52$
139 Fig. 2.24	Softening Point
166 Area of tubes	$\frac{Q_r}{\dots \times 17 \times 10^4} = \text{No. of tubes}$
192 Total Salt	$\frac{10^5 \times 17}{35.5} + 68.6$
197 Problem 3.8	Tables 3.5 & 3.6 under the problem.
222 4th line	2.21 million cubic meters
266 Critical packing size	2.24 $(\gamma/\Delta\rho)^{0.5}$

